**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**

WASHINGTON, D.C. 20460



OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

**MEMORANDUM**

Date: 14-SEP-2006

Subject: Diflubenzuron. IR-4's Request To Register New Food/Feed Uses on Barley, Oats, Wheat, *Brassica* Leafy Greens (Crop Subgroup 5B), Turnip Greens, Eggplant, Okra, Peanut, and Pummelo. **Summary of Analytical Chemistry and Residue Data.** PP#s 5E6965, 5E6966, and 5E6967.

| | | | |
|---|---|---|---|
| DP#s: | 321623, 321625, and 321627 | Decision #s: | 359314, 359335, and 359336 |
| PC Code: | 108201 | MRID #s.: | 46609401, 46609501, and 46609601 |
| 40 CFR §180. | 377 | | |
| Chemical Family: | Urea Derivative | | |

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This document was originally prepared under contract by Dynamac Corporation (2275 Research Blvd, Suite 300; Rockville, MD 20850; submitted 06/23/2006). The document has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## Executive Summary

Diflubenzuron (*N*-[((4-chlorophenyl)amino)carbonyl]-2,6-difluorobenzimide), a member of the urea-derivative chemical family, is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. The Interregional Research Project No. 4 (IR-4), in cooperation with Crompton Corporation, has submitted several petitions for the establishment of permanent diflubenzuron tolerances on several raw agricultural and processed commodities.

Under PP#5E6965, IR-4 requests the establishment of tolerances for the combined residues of diflubenzuron and its metabolites 4-chlorophenylurea (CPU) and 4-chloroaniline (PCA) in/on the following raw agricultural commodities (RACs):

Barley, grain ..... 0.06 ppm

| | |
|---|---|
| Oat, grain | 0.06 ppm |
| Wheat, grain | 0.06 ppm |
| Barley, forage | 5.0 ppm |
| Oat, forage | 5.0 ppm |
| Wheat, forage | 5.0 ppm |
| Barley, hay | 2.0 ppm |
| Oat, hay | 2.0 ppm |
| Wheat, hay | 2.0 ppm |
| Barley, straw | 2.0 ppm |
| Oat, straw | 2.0 ppm |
| Wheat, straw | 2.0 ppm |
| Grain, aspirated fractions | 3.0 ppm |
| Pummelo | 0.5 ppm |

Under PP#5E6966, IR-4 requests the establishment of tolerances for the combined residues of diflubenzuron and its metabolites CPU and PCA, expressed as parent diflubenzuron, in/on the following RACs:

| | |
|---|---|
| *Brassica*, leafy greens, subgroup 5B | 8.0 ppm |
| Turnip greens | 8.0 ppm |
| Eggplant | 1.0 ppm |
| Okra | 1.0 ppm |

Lastly, under PP#5E6967, IR-4 requests the establishment of tolerances for the combined residues of diflubenzuron and its metabolites CPU and PCA, expressed as parent diflubenzuron, in/on the following raw agricultural and processed commodities:

| | |
|---|---|
| Peanut | 0.2 ppm |
| Peanut, hay | 20.0 ppm |
| Peanut, refined oil | 0.2 ppm |

The data package for the current petitions includes magnitude of the residue studies on barley, wheat, peanuts, and mustard greens as well as processing studies on peanuts and wheat. These studies have been reviewed by HED, and the Executive Summaries from the individual Data Evaluation Records (DERs) are incorporated in this summary document. No residue data were submitted for some commodities, and the petitioner requests translation of the available/submitted data: (i) from barley and wheat to oats; (ii) from grapefruit, orange (sweet), and tangerine to pummelo; and (iii) from peppers to eggplant and okra.

IR-4 proposes to add new food/feed uses on the following diflubenzuron end-use products: Dimilin® 2L (EPA Reg. No. 400-461, a flowable concentrate formulation containing 2 lb ai/gal), Dimilin® 25W (EPA Reg. No. 400-465, a wettable powder formulation containing 25% ai), and Micromite® 80WGS (EPA Reg. No. 400-487, 80%, a water-dispersible granule formulation containing 80% ai.

Dimilin® 2L is proposed for use on: (i) barley, oats, triticale, and wheat for a maximum of one foliar application per growing season at 0.0625 lb ai/A with a preharvest interval (PHI) of 45 days for grain and straw; (ii) *Brassica* leafy greens and turnip greens for up to 4 foliar

applications at 0.0625 lb ai/A/application for a seasonal rate of 0.25 lb ai/A with a 7-day PHI; and (iii) peanuts for up to 3 foliar applications at 0.125 lb ai/A/application for a seasonal rate of 0.375 lb ai/A with a 28-day PHI. Dimilin® 25W is proposed for use on eggplant and okra for multiple foliar applications at a maximum single application rate of 0.125 lb ai/A/application and a maximum seasonal rate of 0.375 lb ai/A with a 7-day PHI. Micromite® 80WGS is proposed for use on pummelos for up to 3 foliar applications at 0.3125 lb ai/A/application for a seasonal rate of 0.9375 lb ai/A with a 21-day PHI. Ground and/or aerial applications may be used for the above crops except on *Brassica* leafy greens, turnips greens, eggplant, and okra where applications may only be made by ground equipment. The proposed use of Dimilin® 2L on barley, oats, triticale, and wheat also specifies that the formulation may also be applied by ultra-low-volume (ULV) equipment.

Tolerances for residues of diflubenzuron are established under 40 CFR §180.377. Tolerances listed in 40 CFR §180.377(a)(1) are expressed in terms of diflubenzuron *per se*. Under this section, the listed tolerances are: (i) 0.05 ppm for residues in/on eggs, milk, and the fat and meat of cattle, goat, hog, horse, poultry, and sheep, and for the meat byproducts of poultry; (ii) 0.2 ppm for residues in/on undelinted cottonseed and mushroom; (iii) 0.5 ppm for residues in/on grapefruit, orange (sweet), tangerine, and soybean hulls; and (iv) 6.0 ppm for residues in/on globe artichoke.

Tolerances listed in 40 CFR §180.377(a)(2) are expressed in terms of the combined residues of diflubenzuron and its metabolites CPU and PCA. Under this section, the listed tolerances are: (i) 0.02 ppm for residues in/on rice grain; (ii) 0.06 ppm for residues in/on tree nuts (group 14) and pistachios; (iii) 0.07 ppm for residues in/on fruit, stone (group 12) except cherry; (iv) 0.15 ppm for residues in/on the meat byproducts of cattle, goat, hog, horse, and sheep; (v) 0.50 ppm for residues in/on pear; (vi) 0.8 ppm for residues in/on rice straw; (vii) 1.0 ppm for residues in/on pepper; and (viii) 6.0 ppm for residues in/on almond hulls.

Time-limited tolerances listed in 40 CFR §180.377(b) are expressed in terms of the combined residues of diflubenzuron and its metabolites CPU and PCA, expressed as the parent diflubenzuron, in connection with use of the pesticide under Section 18 Emergency Exemptions granted by EPA. Under this section, the listed tolerances are: (i) 0.05 ppm for residues in/on barley grain and wheat grain; (ii) 0.10 ppm for residues in/on wheat milled byproducts; (iii) 0.50 ppm for residues in/on barley straw and wheat straw; (iv) 1.0 ppm for residues in/on barley hay and wheat hay; (v) 6.0 ppm for residues in/on alfalfa forage and alfalfa hay; and (vi) 30 ppm for residues in/on wheat aspirated grain fractions. Tolerances for alfalfa commodities will expire 6/30/2007 and tolerances for barley and wheat commodities will expire 12/31/08.

The qualitative nature of the residue in plants and fungi is adequately understood based on data from citrus, mushroom, rice, and soybean metabolism studies. The metabolism of diflubenzuron in crops tested is similar, and the radioactive components are also similar to those found in soil. The nature of the residue in livestock is also adequately understood based on acceptable poultry and ruminant metabolism studies reflecting oral dosing. The HED Metabolism Assessment Review Committee (MARC) has concluded that the residues of concern in plants, livestock, and fungi, for the purpose of tolerance expression, are diflubenzuron and its metabolites PCA and CPU.

The nature of the residue in rotational crops is adequately understood for purposes of

reregistration (Residue Chemistry Chapters for the Reregistration Eligibility Decision (RED) document, 3/15/95). The Residue Chapter concluded that although the available confined rotational crop study was inadequate to fully satisfy reregistration requirements, another confined rotational crop study will not be requested because the study allowed HED to make regulatory conclusions regarding the need for limited rotational-crop studies and to comment on the appropriateness of the currently established plantback interval (PBI) on diflubenzuron end-use product labels.

An acceptable limited field rotational crop study has been submitted. HED's review of the study concluded that quantifiable residues of diflubenzuron, CPU and PCA are unlikely to occur in rotated crops planted at least 30 days following treatment at the proposed rate. The petitioner's proposed PBI of 30 days is appropriate.

There are adequate enforcement methods, published in the Pesticide Analytical Manual (PAM, Vol. II), for determining diflubenzuron residues of concern. In addition, a new analytical methodology for plant commodities was successfully validated by an independent laboratory as well as by Agency chemists at the Analytical Chemistry Branch (ACB)/Biological and Economics Analysis Division (BEAD) in conjunction with the approved rice petition (PP#8F4925). The new methods were forwarded to the Food and Drug Administration (FDA) for publication in PAM Vol. II as Roman Numeral Methods. These methods can separately determine residues of diflubenzuron by gas chromatography/electron-capture detection (GC/ECD), CPU by GC/ECD, and PCA by GC/mass spectrometry (MS). The reported limit of quantitation (LOQ) for diflubenzuron in/on rice grain, straw, and bran is 0.01 ppm, and is 0.05 ppm in/on rice hull. In rice straw, the LOQ for CPU is 0.01 ppm and 0.005 ppm for PCA.

Samples of raw agricultural and processed commodities, collected from the field, processing, and storage stability studies, were separately analyzed for residues of diflubenzuron, CPU, and PCA using methods, which are similar or based on method submissions previously deemed acceptable by HED. The data-collection methods were adequately validated, and method recoveries were generally within the acceptable range of 70-120%.

The submitted storage stability data indicate that diflubenzuron is reasonably stable in/on the RACs of barley, wheat, peanut, and mustard greens as well as in the processed commodities of peanut. However, CPU exhibited instability in a few commodities and PCA exhibited instability in many commodities. The storage stability studies suggest that residues of CPU and PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of CPU and PCA residues for degradation during storage would not have a significant effect on the results of the submitted field trials because individual residues of the metabolites in/on treated RAC samples were mostly below the respective LOQs.

Additional storage stability data for wheat processed commodities (except bran) are requested to validate the storage conditions and intervals of samples from the submitted wheat processing study.

There are ruminant and/or poultry feed items associated with the proposed uses of diflubenzuron on barley, oats, wheat, and peanuts. The calculated maximum theoretical dietary burdens (22.2 ppm for beef cattle, 34.8 ppm for dairy cattle, 0.052 ppm for poultry, and 0.058 ppm for hog),

resulting from the proposed/registered uses, are supported by previously submitted livestock feeding studies. HED concludes that the current tolerances on meat, milk, poultry, and eggs are adequate to cover the added residues resulting from the proposed uses.

Adequate magnitude of the residue data have been submitted for barley grain, barley hay, barley straw, wheat grain, wheat forage, wheat hay, and wheat straw. These data were generated from field trials using spray volumes of 10-20 gallons per acre using ground equipment. The petitioner should delete the proposed application method using ULV (24-32 fl. oz/A) equipment. Barley forage is not listed in Table 1 of OPPTS 860.1000 and should be removed from the petitioner's Section F. As the proposed use is geographically limited, the available data for wheat may be translated to oats; the corresponding tolerances recommended for wheat commodities also apply to oat commodities. The proposed use on triticale is supported by the submitted data for wheat as per 40 CFR 180.1.

The established grapefruit tolerance may be used to support the requested tolerance of 0.5 ppm on pummelos.

Adequate magnitude of the residue data have been submitted for mustard greens, the representative commodity of the *Brassica* leafy greens (subgroup 5B).

Turnip greens will be removed from Crop Group 2: Leaves of root and tuber vegetables group, and will become a member of Crop Subgroup 5B: Leafy *Brassica* greens (Reviewer's Guide and Summary..., B. Schneider, 6/14/02). Forage turnip varieties grown for livestock feed uses only will remain in Crop Group 2: Leaves of root and tuber vegetables group. As mustard greens are the representative commodity of the *Brassica* leafy greens (subgroup 5B), the mustard green residue data can be translated to turnip greens. However, the label should be amended to prohibit use on dual purpose turnip cultivars or varieties which produce a harvestable root.

No residue data were submitted in support of the proposed uses on okra or eggplant. The petitioner requests translation of the available data from pepper to okra and eggplant. However, HED does not generally translate residue data among members of a crop group unless a crop group tolerance is established. Thus, the proposed tolerances for okra and eggplant should be withdrawn and the use directions for okra and eggplant removed from the label until adequate okra and eggplant residue data are available or a crop group tolerance for fruiting vegetables is established.

The submitted data for peanut nutmeat and peanut hay are inadequate because geographic representation of residue data is insufficient as the results from three trials were invalidated because of possible sample contamination. Confirmatory residue data from an additional three peanut field trials conducted in Zone 2 are requested.

The submitted peanut processing study is inadequate because the study has not definitively proven that diflubenzuron residues of concern will not concentrate in the processed commodities of peanuts as a result of the proposed use. A new peanut processing study is requested.

The submitted wheat processing study is not supported by adequate storage stability data, and these data are requested. Although inadequate, the study indicates that the combined residues of diflubenzuron and its CPU and PCA metabolites do not appear to concentrate in shorts,

middlings, flour, bran, and germ processed from wheat grain treated at 1x and 10x the field rate. The combined residues, however, concentrated >35x and 180x in aspirated grain fractions processed from wheat grain treated at 1x and 10x, respectively.

## REGULATORY RECOMMENDATIONS

PP#5E6965: Provided revised Sections B and F are submitted, HED concludes there are no residue chemistry data requirements that would preclude the establishment of the HED-recommended tolerances for diflubenzuron in/on the relevant commodities as specified in Table 12. The proposed uses of Dimilin® 2L on barley, oats, triticale, and wheat should be made conditional upon resolving the storage stability deficiencies cited below. The proposed use of Micromite® 80WGS on pummelos can be unconditional.

PP#5E6966: Provided revised Sections B and F are submitted, HED concludes there are no residue chemistry data requirements that would preclude the establishment of the HED-recommended tolerances as specified in Table 12 and unconditional registration for diflubenzuron on *Brassica* leafy greens (subgroup 5B) and turnip greens.

PP#5E6967: Provided a revised Section F is submitted, HED concludes there are no residue chemistry data requirements that would preclude the establishment of the HED-recommended tolerances for diflubenzuron in/on the relevant commodities as specified in Table 12. The proposed use of Dimilin® 2L on peanuts should be made conditional upon submission of additional field trial and processing data as cited below.

## RESIDUE CHEMISTRY DEFICIENCIES

860.1200 Directions for Use

- Barley, oats, and wheat: The petitioner should delete the proposed application method using ULV (24-32 fl. oz/A) equipment. Label revisions are requested to specify appropriate PHIs based on the reviewed data. Labels should be revised to specify PHIs of 50 days for grain and straw, 3 days for forage, and 15 days for hay.

- Turnip greens: The label should be amended to prohibit use on dual purpose turnip cultivars or varieties which produce a harvestable root.

- Okra and eggplant: The use directions for okra and eggplant should be removed from the label.

860.1380 Storage Stability

- Barley, oats, and wheat: Additional storage stability data for wheat processed commodities (except bran) are requested to validate the storage conditions and intervals of samples from the submitted wheat processing study. The available storage stability data for rice bran may be translated to wheat bran; the petitioner is only requested to generate storage stability data for wheat flour, middlings, shorts, and germ. The requested data should reflect the storage conditions and intervals of samples from the wheat processing study.

860.1500 Crop Field Trials

- Peanut: Confirmatory residue data on peanut nutmeat and peanut hay are requested from three additional field trials conducted in Zone 2.

860.1520 Processed Food/Feed

- Peanut: A new peanut processing study is requested using a minimum seasonal rate of ≥3x, which is the maximum theoretical concentration factor (by crop) for peanuts. The meal samples from this study should be analyzed with a method which has a LOQ for diflubenzuron which is comparable to that of the RAC (0.05 ppm).

860.1550 Proposed Tolerances

- Barley, oats, and wheat: A revised Section F should be submitted to reflect HED-recommended tolerance levels of 3.0 ppm for residues in/on barley hay, 1.8 ppm for residues in/on barley straw, 7.0 ppm for residues in/on wheat forage, 6.0 ppm for residues in/on wheat hay, 3.5 ppm for residues in/on wheat straw, and 11 ppm for residues in/on aspirated grain fractions. Barley forage is not listed in Table 1 of OPPTS 860.1000; therefore, this entry should be removed from the petitioner's Section F. The available data for wheat may be translated to oats; the corresponding tolerances recommended for wheat commodities also apply to oat commodities.

- *Brassica* leafy greens: A revised Section F should be submitted to reflect HED-recommended tolerance level of 9.0 ppm for residues in/on *Brassica* leafy greens, subgroup 5B.

- Peanut: A revised Section F should be submitted to reflect HED-recommended tolerance levels of 0.10 ppm for residues in/on peanut, 55 ppm for residues in/on peanut hay, and 0.20 ppm for residues in/on peanut oil.

- Mustard greens: A revised Section F should be submitted to reflect HED-recommended tolerance level of 9.0 ppm.

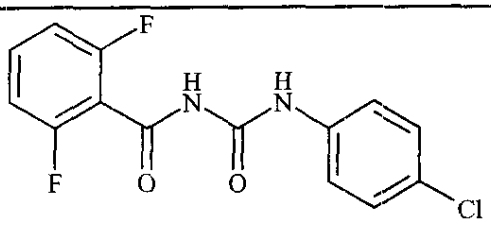
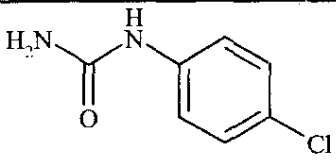
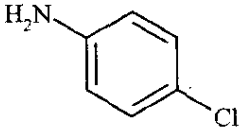
- Okra and eggplant: The proposed tolerances for okra and eggplant should be withdrawn.

**A human-health risk assessment will be prepared as a separate document.**

**Background**

Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The RED for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008).

The chemical structure and nomenclature of diflubenzuron are presented in Table 1. The physicochemical properties of the technical grade of diflubenzuron are presented in Table 2.

| **Table.1. Diflubenzuron Nomenclature.** | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | Dimilin, Vigilante, Micromite, Adept |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Products (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461);<br>25% WP formulation; DIMILIN® 25W (EPA Reg. No. 400-465);<br>80% G formulation; Micromite® 80WGS (EPA Reg. No. 400-487); |
| Regulated Metabolite |  |
| Common name | 4-chlorophenylurea (CPU) |
| Regulated Metabolite |  |
| Common Name | 4-chloroaniline (PCA) |

| **Table 2. Physicochemical Properties of Diflubenzuron.** | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | Not available | |
| Density | Not available | |
| Water solubility (25 °C) | 0.08 ppm | |
| Solvent solubility (25 °C) (ppm) | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25 °C) | $1.2 \times 10^{-4}$ mPa | |
| *Dissociation constant*, $pK_a$ | Not available | |
| Octanol/water partition coefficient, Log($K_{OW}$) | 3.89 | |
| UV/visible absorption spectrum | Not available | |

## 860.1200 Directions for Use

A summary of the proposed end-use products is presented in Table 3. Table 4 lists the summary of proposed use patterns.

**Table 3. Summary of Proposed End-Use Products.**

| Trade Name | Reg. No. | % ai (formulation) | Formulation Type | Target New Crops | Target Pests | Label Date |
|---|---|---|---|---|---|---|
| Dimilin® 2L | 400-461 | 22% (2 lb ai/gal) | Flowable concentrate (FlC) | Barley, oats, triticale, and wheat, peanut, leafy *Brassica*, and turnip greens | Grasshoppers, cereal leaf beetle, velvet bean caterpillar, Mexican bean beetle, green clover worm, armyworms, lesser cornstalk borer, soybean looper (suppression) | Undated specimen label |
| Dimilin® 25W | 400-465 | 25% | Wettable powder (WP) | Eggplant and okra | Foliage-feeding Lepidopteran insects | Undated specimen label |
| Micromite® 80WGS | 400-487 | 80% | Water-dispersible granule | Pummelos | Citrus rust mite, Lepidopterous miners, and citrus root weevil complex | Undated specimen label |

**Table 4. Summary of Proposed Directions for Use of Diflubenzuron.**

| Applic. Timing, Type, Equipment. | Formulation [EPA Reg. No.] | Applic. Rate (lb ai/A) | Max. No. Applic. per Season | Max. Seasonal Applic. Rate (lb ai/A) | PHI (days) |
|---|---|---|---|---|---|
| **Barley, Oats, Triticale, and Wheat** | | | | | |
| Foliar prior to boot stage<br>ULV (24-32 fl. oz/A)<br>Aerial (3-5 GPA)<br>Ground (5-15 GPA) | Use Directions and Limitations: Use limited to crops grown in Alaska, Colorado, Idaho, Montana, Nevada, Oregon, Utah, Washington, Wyoming, Western North and South Dakota, and Western Nebraska (West of Route 281 in ND, SD, & NE). Do not apply after boot stage of growth. For control of grasshoppers, apply when pests have reached the 2nd to 3rd nymphal stage of development. For control of cereal leaf beetle, apply at first sign of egg laying. | | | | |
| | 2 lb/gal FlC [400-461] | 0.0625 | 1 | 0.0625 | 45 for grain and straw |
| ***Brassica* Leafy Greens including Mustard Greens; *Turnip* Greens** | | | | | |
| Foliar<br>Ground (Min 30 GPA) | Use Directions and Limitations: For control of grasshoppers, apply when pests have reached the 2nd to 3rd nymphal stage of development. Reapply in 7-10 day intervals if nymphal hatchout or crop re-infestations continue. | | | | |
| | 2 lb/gal FlC [400-461] | 0.0625 | 4 | 0.25 | 7 |
| **Eggplant** | | | | | |
| Foliar<br>Ground (Min 30 GPA) | Use Directions and Limitations: Allow a minimum of 7 days between any 2 applications. | | | | |
| | 25% WP [400-465] | 0.125 | Up to 5 treatments may be made as long as the maximum seasonal rate of 0.375 lb ai/A is not exceeded. | | 7 |
| **Okra** | | | | | |
| Foliar<br>Ground (Min 30 GPA) | Use Directions and Limitations: Allow a minimum of 7 days between any 2 applications. | | | | |
| | 25% WP [400-465] | 0.125 | Up to 5 treatments may be made as long as the maximum seasonal rate of 0.375 lb ai/A is not exceeded. | | 7 |

| Table 4. Summary of Proposed Directions for Use of Diflubenzuron. | | | | | |
|---|---|---|---|---|---|
| Applic. Timing, Type, Equipment. | Formulation [EPA Reg. No.] | Applic. Rate (lb ai/A) | Max. No. Applic. per Season | Max. Seasonal Applic. Rate (lb ai/A) | PHI (days) |
| **Peanut** | | | | | |
| Foliar<br>Aerial (3-5 GPA)<br>Ground (10-20 GPA) | Use Directions and Limitations: Allow at least 14 days between any two applications. Repeat applications if the egg laying period is lengthy and/or another pest infestation occurs. | | | | |
| | 2 lb/gal FlC [400-461] | 0.125 | 3 | 0.375 | 28 |
| **Pummelo** | | | | | |
| Foliar<br>Aerial (5-20 GPA)<br>Ground (50-1,000 GPA) | Use Directions and Limitations: Maintain a minimum of 90 days between applications. Do not harvest cover crops for livestock feed or graze livestock in treated groves. | | | | |
| | 80% WGS [400-487] | 0.3125 | 3 | 0.9375 (max yearly rate) | 21 |

The following rotational crop restriction is specified on the undated draft specimen labels of the 2 lb/gal FlC (Dimilin® 2L; EPA Reg. No. 400-461) and 25% WP (Dimilin® 25W; EPA Reg. No. 460-465) formulations: "Do not plant food or feed crops in DIMILIN treated soils within 1 month following last application, unless DIMILIN is authorized for use on these crops."

*Conclusions*. The submitted labels are adequate to allow evaluation of the residue data relative to the proposed uses except: Barley, oats, and wheat: The petitioner should delete the proposed application method using ULV (24-32 fl. oz/A) equipment. Label revisions are requested to specify appropriate PHIs based on the reviewed data. Labels should be revised to specify PHIs of 50 days for grain and straw, 3 days for forage, and 15 days for hay. Turnip greens: The label should be amended to prohibit use on dual purpose turnip cultivars or varieties which produce a harvestable root. Okra and eggplant: The use directions for okra and eggplant should be removed from the label. **Revised Section Bs should be submitted.**

## 860.1300 Nature of the Residue – Plants, Livestock & Fungi

Summary of Plant Metabolism Studies (DP# 272978, G. Kramer, 4/3/2001)
HED Metabolism Assessment Review Committee (MARC) Meetings of 2/20/2001 and 5/8/2001.
Residues of Concern for Cancer Risk Assessment (DP# 272976, G. Kramer and G. Reddy, 5/31/2001)

The qualitative nature of the residue in plants, livestock and fungi is adequately understood based on data from citrus, mushroom, rice, soybean, poultry, and ruminant metabolism studies. The HED MARC has concluded that the residues of concern are diflubenzuron and its metabolites PCA and CPU.

## 860.1340 Residue Analytical Methods

Tolerance enforcement methods

Residue Chemistry Chapter of the Diflubenzuron RED (DP# 209032, S. Knizner, 3/15/1995)
DP# D285141 (G. Kramer, 9/6/2002)

Three enforcement methods for diflubenzuron are published in the Pesticide Analytical Manual

(PAM, Vol. II) as Methods I, II, and III. Method I is a GC/ECD method that determines diflubenzuron in plants as derivatized PCA. Method II is a GC/ECD method that can separately determine residues of diflubenzuron, CPU and PCA in eggs, milk, and livestock tissues, each as derivatized PCA. Method III is a high-performance liquid chromatography/ultraviolet (HPLC/UV) method that determines diflubenzuron *per se* in eggs, milk, and livestock tissues. All three methods have undergone successful Agency validations. The Diflubenzuron RED stated that Methods I and II are the preferred enforcement methods because they are easier to perform, have less interference, and are more sensitive.

In conjunction with the approved rice petition (PP#8F4925), a new analytical methodology for plant commodities was successfully validated by an independent laboratory as well as by Agency chemists at ACB/BEAD, and was forwarded to FDA for publication in PAM Vol. II as Roman Numeral Methods. These methods can separately determine residues of diflubenzuron by GC/ECD, CPU by GC/ECD, and PCA by GC/MS using an isotopically labeled internal standard and by summing the response of the two ions. The reported LOQ for diflubenzuron in/on rice grain, straw, and bran is 0.01 ppm, and is 0.05 ppm in/on rice hull. In rice straw, the LOQ for CPU is 0.01 ppm and 0.005 ppm for PCA.

Data-collection methods

Samples of raw agricultural and processed commodities, taken from the field, processing, and storage stability studies were separately analyzed for residues of diflubenzuron, CPU, and PCA using methods, which are similar or based on method submissions previously deemed acceptable by HED. The data-collection methods were adequately validated, and method recoveries were generally within the acceptable range of 70-120%. Complete descriptions of these methods along with method recoveries are presented in the individual study DERs.

### 860.1360 Multiresidue Methods

PAM Vol. I, Appendix II
DP# 194722, L. Edwards, 9/17/93: Transmission of MRM data for diflubenzuron to FDA.
DP# 254273, J. Rowell, 12/15/1998: Transmission of MRM data for PCA and CPU to FDA

The FDA PESTDATA database dated 1/94 (PAM Vol. I, Appendix II) contain no information on diflubenzuron recovery using Multiresidue Methods PAM, Vol. I Sections 302, 303, and 304. However, the registrant has submitted Multiresidue testing data for diflubenzuron that HED has forwarded to the FDA. In addition, the results of Multiresidue Method testing of PCA and CPU have been submitted and forwarded to FDA. Neither PCA nor CPU was adequately recovered.

### 860.1380 Storage Stability

The storage intervals and conditions of samples from the crop field trials and processing studies submitted to support these petitions are presented in Table 5.

| Table 5. Storage Conditions and Intervals of Samples from Crop Field Trial and Processing Studies. | | | |
|---|---|---|---|
| Matrix | Storage Temperature (°C) | Actual Storage Duration (Days) | Interval of Demonstrated Storage Stability |
| **Barley and Wheat Field Trials (MRID 46609501)** | | | |
| Grain | <0 | 169-189 | Diflubenzuron is stable in barley grain for 296 days, barley straw for 301 days, wheat forage for 422 days, and wheat hay for 337 days. CPU is stable in barley grain for 348 days and wheat forage for 267 days but showed a decline in barley straw after 299 days and in wheat hay after 355 days. PCA was reasonably stable in barley straw after 302 days, marginally stable in wheat hay after 359 days, and unstable in barley grain and wheat forage after 345 days. |
| Straw | <0 | 166-232 | |
| Forage | <0 | 183-262 | |
| Hay | <0 | 205-245 | |
| **Wheat Processing Study (MRID 46609501)** | | | |
| Wheat grain | <0 | 100-105 | Diflubenzuron is stable for 296 days, CPU for 348 days, and PCA for 293 days in the RAC (wheat grain). |
| Shorts | <0 | 90-113 | The available storage stability data (DP# 244487, G. Kramer, 2/17/1999) for rice bran may be translated to wheat bran. |
| Middlings | <0 | 90-113 | |
| Flour | <0 | 96-111 | |
| Bran | <0 | 92-98 | |
| Germ | <0 | 96-321 | |
| Aspirated Grain | <0 | 92-98 | |
| **Mustard Greens Field Trials (MRID 46609601)** | | | |
| Mustard greens | <0 | 422-520 | Diflubenzuron is stable in mustard greens for up to 422 days and CPU for up to 520 days. PCA was unstable after 423 days of storage. |
| **Peanut Field Trials (MRID 46609401)** | | | |
| Peanut nutmeat | <0 | 244-408 | Diflubenzuron is stable in nutmeat for up to 295 days; however, CPU and PCA exhibited 33-37% reduction in residues after 421 and 289 days. A similar profile was observed for peanut hay. Diflubenzuron is stable in hay for up to 356 days; CPU and PCA exhibited 25-71% reduction in residues after 484 and 338 days of frozen storage, respectively. |
| Peanut hay | <0 | 323-481 | |
| **Peanut Processing Study (MRID 46609401)** | | | |
| Peanut meal | <0 | 254-639 | Diflubenzuron is stable in meal and oil fortified at 0.5 ppm and stored for 643 and 365 days, respectively. CPU is stable in meal and oil stored 645 and 294 days, respectively. PCA is stable in meal and oil stored 488 and 286 days, respectively. |
| Peanut oil | <0 | 252-276 | |

Storage stability data

DP 244487; G. Kramer, 2/17/1999

To validate sample storage conditions and intervals, the petitioner included storage stability data in the respective magnitude of the residue study submissions. These data are summarized below.

The submitted storage stability study for small grains indicate that diflubenzuron is reasonably stable in barley grain for 296 days, barley straw for 301 days, wheat forage for 422 days, and

wheat hay for 337 days. CPU was reasonably stable in barley grain for 348 days and wheat forage for 267 days but showed a decline in barley straw (average corrected stored recovery of 34%) after 299 days and in wheat hay (average corrected stored recovery of 30%) after 355 days. PCA was reasonably stable in barley straw after 302 days, marginally stable in wheat hay after 359 days, and unstable in barley grain (average corrected stored recovery of 33%) and wheat forage (average corrected stored recovery of 39%) after 345 days.

No storage stability data for wheat processed commodities are available. The available storage stability data for rice processed commodities may be translated to wheat processed fractions. These data indicate that diflubenzuron and CPU are stable in the processed commodities of rice over a 12-month period. PCA is unstable, degrading significantly after 1 month.

The submitted storage stability data for mustard greens show that diflubenzuron is reasonably stable in frozen mustard greens for up to 422 days. CPU was also found to be stable in frozen mustard greens for up to 520 days. However, residues of PCA were unstable (average corrected stored recovery of 17%) after 423 days of storage.

The submitted storage stability data for peanuts indicate that diflubenzuron is relatively stable in/on nutmeat for up to 295 days; however, CPU (average corrected stored recovery of 67%) and PCA (average corrected stored recovery of 63%) exhibited 33-37% reduction in residues after 421 and 289 days of frozen storage, respectively. A similar storage stability profile was observed for peanut hay. Diflubenzuron is relatively stable in/on hay for up to 356 days; CPU (average corrected stored recovery of 29%) and PCA (average corrected stored recovery of 75%) exhibited 25-71% reduction in residues after 484 and 338 days of frozen storage, respectively.

The submitted storage stability data for peanut processed commodities indicate that diflubenzuron is stable in meal and oil fortified at 0.5 ppm and stored for 643 and 365 days, respectively. CPU is stable in meal and oil stored for 645 and 294 days, respectively. PCA is stable in meal and oil stored for 488 and 286 days, respectively.

*Conclusions*: The submitted storage stability data indicate that diflubenzuron is reasonably stable in/on the RACs of barley, wheat, peanut, and mustard greens as well as the in the processed commodities of peanut. However, CPU exhibited instability in a few commodities and PCA exhibited instability in many commodities. The storage stability studies suggest that residues of CPU and PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of CPU and PCA residues for degradation during storage would not have a significant effect on the results of the submitted field trials because individual residues of the metabolites in/on treated RAC samples were mostly below the respective LOQs.

Additional storage stability data for wheat processed commodities (except bran) are requested to validate the storage conditions and intervals of samples from the submitted wheat processing study. The available storage stability data for rice bran may be translated to wheat bran; the petitioner is only requested to generate storage stability data for wheat flour, middlings, shorts, and germ.

## 860.1480 Meat, Milk, Poultry, and Eggs

Maximum Theoretical Dietary Burdens (MTDB)

There are ruminant and/or poultry feed items associated with the proposed uses of diflubenzuron on barley, oats, wheat, and peanuts. Although there are many plausible ways of estimating the MTDB of diflubenzuron to livestock, the calculation of dietary burdens, presented in Table 6, largely incorporates the feed items associated with these petitions. The calculated dietary burdens should be considered tentative because additional field trial data are being requested for some commodities including peanut hay; a new peanut processing study is also requested. The MTDBs of diflubenzuron are 22.2 ppm for beef cattle, 34.8 ppm for dairy cattle, 0.052 ppm for poultry, and 0.058 ppm for hog.

**Table 6. Calculation of Maximum Theoretical Dietary Burdens of Diflubenzuron Residues to Livestock.**

| Feedstuff | % Dry Matter[1] | % Diet[1] | Recommended Tolerance (ppm) | Dietary Contribution (ppm)[2] |
|---|---|---|---|---|
| **Beef Cattle** | | | | |
| Peanut hay | 85 | 25 | 55[3] | 16.2 |
| Wheat grain | 89 | 50 | 0.06 | 0.03 |
| Grass forage | 25 | 25 | 6.0 | 6.00 |
| TOTAL BURDEN | | 100 | | **22.2** |
| **Dairy Cattle** | | | | |
| Peanut hay | 85 | 50 | 55[3] | 32.4 |
| Wheat grain | 89 | 40 | 0.06 | 0.03 |
| Grass forage | 25 | 10 | 6.0 | 2.40 |
| TOTAL BURDEN | | 100 | | **34.8** |
| **Poultry** | | | | |
| Wheat grain | 89 | 80 | 0.06 | 0.048 |
| Rice grain | 88 | 20 | 0.02 | 0.004 |
| TOTAL BURDEN | | 100 | | **0.052** |
| **Hog** | | | | |
| Wheat grain | 89 | 80 | 0.06 | 0.048 |
| Soybean seed | 89 | 20 | 0.05 | 0.010 |
| TOTAL BURDEN | | 100 | | **0.058** |

[1] Table 1 (OPPTS Guideline 860.1000).

[2] Contribution = ([tolerance /% DM] X % diet) for beef and dairy cattle; contribution = ([tolerance] X % diet) for poultry and hog.

[3] Tentatively assessed tolerance level for peanut hay based on input of limited residue data into HED's Tolerance Spreadsheet; additional confirmatory field trials on peanuts are requested.

Livestock Feeding Studies

Residue Chemistry Chapter of the Diflubenzuron Registration Standard (11/84)
Residue Chemistry Chapter of the Diflubenzuron RED (DP# 209032, S. Knizner, 3/15/1995)

No livestock feeding studies were submitted with these petitions. Numerous diflubenzuron feeding studies have been reviewed previously by HED. Those that are the most relevant to the current petitions are discussed below.

In one cattle study, lactating cows were dosed orally twice a day with diflubenzuron at either 25 (0.7x) or 250 (7x) ppm in the diet for up to 28 consecutive days. Residues of diflubenzuron *per se* were nondetectable (<0.05 ppm) in milk from both feeding levels sampled following 1 to 28 days of dosing. Residues of diflubenzuron *per se* were also nondetectable (<0.05 ppm) in the fat, muscle, liver, and kidneys of cows sacrificed after 8, 18, and 28 days of dosing at 25 (0.7x) ppm. For cows sacrificed after dosing at 250 (7x) ppm for 8, 18 and 28 days, residues of diflubenzuron *per se* were nondetectable (<0.05 ppm) in the muscle and kidney, 0.06-0.08 ppm in fat, and 0.09-0.1 ppm in liver.

In the third study, four dairy calves were fed diflubenzuron at a rate of 2.8 mg ai/kg body weight for 4-5 months and two were sacrificed. Then three others were fed at 1 mg ai/kg body weight for another year and sacrificed. The 2.8 and 1.0 mg/kg doses were equivalent to approximately 180 (5x) and 65 (2x) ppm, respectively, in the diet. Following dosing at 180 ppm (5x), residues of diflubenzuron were 0.02 ppm in liver and kidney, 0.04-0.08 ppm in fat, and <0.02 ppm in muscle. Residues of diflubenzuron *per se* were nondetectable (<0.02 ppm) in tissues from livestock after dosing at 65 ppm (2x).

Acceptable data are also available for residues of diflubenzuron in eggs, meat, meat byproducts, and fat of poultry. The Residue Chemistry Chapter of the Diflubenzuron Registration Standard (11/84) and the Addendum to the Diflubenzuron Registration Standard (12/84) cited five feeding studies on poultry. In one study, laying hens were orally dosed via capsule for 1-28 consecutive days at 0.05 (1x), 0.5 (10x), and 5 (100x) ppm of [$^{14}$C]diflubenzuron in the diet. Hens were sacrificed at 3- to 7-day intervals throughout the study. Residues of diflubenzuron *per se* were 0.21 ppm in fat after dosing at 5 ppm (100x) for 7 days. After 24 days of dosing at 5 ppm (100x), residues of diflubenzuron *per se* were 0.05 ppm in muscle and kidney, 0.16 ppm in liver, and 0.14 ppm in eggs.

In another study, Black Barred Rock-Rhode Island Red (BBR/RIR) and White Leghorn (WL) hens were given feed containing diflubenzuron at 10 ppm (200x) for 15 weeks. Residues of diflubenzuron *per se* plateaued in eggs after ~2 weeks and remained constant at ~0.3-0.6 ppm for the remainder of the dosing period. Hens were sacrificed after a 3-day withdrawal period. For BBR/RIR hens, average residues of diflubenzuron were 1.17 ppm in fat, 0.12 ppm in liver, and nondetectable (<0.01 ppm) in muscle at the end of the dosing period. For WL hens, average residues of diflubenzuron were 1.85 ppm in fat, 0.45 ppm in liver, and nondetectable (<0.01 ppm) in muscle at the end of the dosing period.

Male Hubbard chickens in another study were dosed for 98 days with feed containing diflubenzuron at 2.5 and 250 ppm, five hens at each level. At the 2.5 ppm feeding level (50x), residues of diflubenzuron *per se* were 2.2-6.9 ppm in fat, 0.09-0.45 ppm in muscle and skin, and 0.06-0.72 ppm in liver. At the 250 ppm feeding level (5000x), residues of diflubenzuron were 23-62 ppm in fat, 0.9-3.3 ppm in muscle and skin, and 0.8-3.8 ppm in liver.

*Conclusions*. There are ruminant and/or poultry feed items associated with the proposed uses of diflubenzuron on barley, oats, wheat, and peanuts. The calculated maximum theoretical dietary burdens (22.2 ppm for beef cattle, 34.8 ppm for dairy cattle, 0.052 ppm for poultry, and 0.058 ppm for hog), resulting from the proposed uses, are supported by previously-submitted livestock feeding studies. HED concludes that the current tolerances on meat, milk, poultry, and eggs are adequate to cover the added residues resulting from the proposed uses.

## 860.1500 Crop Field Trials

Barley and Wheat

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Seven field trials on barley (2 winter and 5 spring varieties) and three trials on wheat (1 winter and 2 spring varieties) were conducted in EPA Zones 5, 7, 8 and 11 between the 2002 and 2003 growing seasons. At each location, diflubenzuron (2 lb/gal FlC) was applied once to barley and wheat fields as a broadcast foliar application at 0.0592-0.0642 lb ai/A (1x) during crop development (pre-boot, pre-stem elongation, jointing, or Feekes 8 growth stage). A single control and duplicate treated samples of mature grain and straw were harvested from each site at 50-76 days after treatment (DAT). Hay was harvested from each site at 15-39 DAT, and wheat forage was harvested at 3-12 DAT. The collected samples of grain, straw, forage, and hay were stored frozen for up to 189, 232, 262 and 245 days, respectively, prior to residue analysis. The storage intervals and conditions are supported by adequate storage stability data.

The harvested commodities of barley and wheat were analyzed for residues of diflubenzuron, CPU, and PCA using HPLC/UV, GC/MS, and GC/MS with selected ion monitoring, respectively. These methods, which are similar or based on method submissions previously deemed acceptable by HED, were adequately validated in conjunction with the field sample analyses. The lowest limit of method validations (LLMV) are 0.05 ppm for diflubenzuron and 0.005 ppm for CPU and PCA.

The results of the field trials (Table 7) indicate that following a single foliar application of the 2 lb/gal FlC formulation, the combined residues of diflubenzuron, CPU and PCA were: 0.13-1.47 ppm in/on barley hay (15-39 day PHI); <0.06 ppm in/on barley grain (50-76 day PHI); <0.06-0.58 ppm in/on barley straw (50-76 day PHI); 1.17-3.97 ppm in/on wheat forage (3-12 day PHI); 0.11-1.31 ppm in/on wheat hay (28-32 day PHI); <0.06 ppm in/on wheat grain (56-62 day PHI); and <0.06-1.04 ppm in/on wheat straw (56-62 day PHI). The combined highest-average field trial (HAFT) values were: 1.40 ppm for barley hay; <0.06 ppm for barley grain; 0.57 ppm for barley straw, 3.80 ppm for wheat forage; 1.28 ppm for wheat hay; <0.06 ppm for wheat grain; and 0.91 ppm for wheat straw.

**Table 7. Summary of Residue Data from Barley and Wheat Field Trials with Diflubenzuron.**

| Commodity | Total Applic. Rate (lb ai/A) | PHI (days) | Combined Residues of Diflubenzuron, CPU, and PCA (ppm)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | N | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Barley, hay | 0.0592-0.0629 | 15-39 | 14 | 0.13 | 1.47 | 1.40 | 0.68 | 0.67 | 0.38 |
| Barley, grain | | 50-76 | 14 | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | 0.0 |
| Barley, straw | | 50-76 | 14 | <0.06 | 0.58 | 0.57 | 0.32 | 0.33 | 0.20 |
| Wheat, forage | 0.0619-0.0642 | 3-12 | 6 | 1.17 | 3.97 | 3.80 | 2.57 | 2.70 | 1.00 |
| Wheat, hay | | 28-32 | 6 | 0.11 | 1.31 | 1.28 | 0.89 | 0.78 | 0.50 |
| Wheat, grain | | 56-62 | 6 | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | 0.0 |
| Wheat, straw | | 56-62 | 6 | <0.06 | 1.04 | 0.91 | 0.30 | 0.43 | 0.40 |

[1] The LLMV is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA.
[2] HAFT = Highest-Average Field Trial.

*Conclusions*: The submitted field trial data for barley and wheat commodities reflect the proposed crop use pattern and are supported by acceptable storage stability data. Samples were analyzed for diflubenzuron residues of concern using adequate data-collection methods.

Geographic representation of residue data is adequate for the purpose of seeking regional registration of diflubenzuron on crops grown in Alaska, Colorado, Idaho, Montana, Nevada, Oregon, Utah, Washington, Wyoming, Western North and South Dakota, and Western Nebraska (West of Route 281 in ND, SD, & NE). Note that HED previously approved the number and location of these field trials (e-mail correspondences between J. Corley of IR-4 and G. Herndon, 11/25/03).

The submitted data for barley grain and wheat grain showed that residues were below the respective LLMVs for each analyte (with a combined LLMV of <0.06 ppm) in/on treated samples. The proposed tolerance of 0.06 ppm for barley grain and wheat grain are appropriate pending label revision to specify a 50-day PHI for barley grain and wheat grain.

The submitted data for the remainder of barley and wheat commodities were entered into the tolerance spreadsheet (see Appendix I). Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, HED recommends tolerance levels of 3.0 ppm for barley hay, 1.8 ppm for barley straw, 7.0 ppm for wheat forage, 6.0 ppm for wheat hay, and 3.5 ppm for wheat straw. Barley forage is not listed in Table 1 of OPPTS 860.1000; therefore, this entry should be removed from the Section F.

Label revisions are requested to specify appropriate PHIs based on the reviewed data. Labels should be revised to specify PHIs of 50 days for grain and straw, 3 days for forage, and 15 days for hay.

The submitted residue data for wheat commodities may be translated to oat commodities because the registered uses on small grains are identical and proposed use is geographically limited. This recommendation is contingent upon the requested label revisions.

The proposed use on triticale is supported by the submitted data for wheat as per 40 CFR 180.1.

Pummelo

No residue data were submitted in support of the proposed tolerance for pummelo. The petitioner requests translation of the available data from citrus fruits to pummelo. As pummelos are to be included in the definition of grapefruit (Reviewer's Guide and Summary..., B. Schneider, 6/14/02), this data translation is appropriate.

*Conclusions*: The established grapefruit tolerance may be used to support the requested tolerance of 0.5 ppm for residues in/on pummelos.

Mustard Greens

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Eight field trials on mustard greens were conducted in EPA Zones 2, 3, 5, 6, and 10 during the 2001 growing season. At each location, diflubenzuron (2 lb/gal FlC) was applied four times (except for one trial site where only three treatments were made) as broadcast foliar applications using ground equipment at 0.061-0.066 lb ai/A/application for a total rate of 0.19-0.26 lb ai/A (0.8-1x). Treatments were made during the crop's vegetative growth stage at a retreatment

interval of 8-15 days. Duplicate control and treated samples of mature mustard greens were harvested from each site at 6-8 DAT. Mustard green samples were stored frozen up to 520 days prior to residue analysis, an interval supported by available storage stability data.

The harvested samples of mustard greens were analyzed for residues of diflubenzuron, CPU, and PCA using HPLC/UV, GC/ECD and GC/MSD methods, respectively. These methods, which are similar or based on method submissions previously deemed acceptable by HED, were adequately validated in conjunction with the field sample analyses. The LOQs are 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA.

The results (Table 8) show that the combined residues of diflubenzuron, CPU, and PCA were <0.065 ppm-7.07 ppm in/on mustard greens harvested 6-8 days following the last of 3 to 4 foliar treatments of a 2 lb/gal FlC test formulation for a total application rate of 0.19-0.26 lb ai/A. The HAFT was 6.85 ppm and the average combined residues were 2.05 ppm.

No residue decline data were submitted. HED generally requires residue decline data when a pesticide is applied when the edible portion of the crop has formed and/or it is clear that quantifiable residues may occur in/on food or feed commodities at the earliest harvest time. However, decline data were previously submitted with the stone fruit residue trials (45252206.der.wpd). These data do demonstrate that residues generally declined from the 14-day PHI to the 28-day PHI. HED is willing to translate these data to mustard greens and concludes that additional residue decline data on mustard greens will not be requested.

**Table 8. Summary of Residue Data from Mustard Green Field Trials with Diflubenzuron.**

| Commodity | Total Applic. Rate (lb ai/A) | PHI (days) | Combined Residues of Diflubenzuron, CPU, and PCA (ppm)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | n | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Mustard Greens | 0.19-0.26 | 6-8 | 16 | <0.065 | 7.07 | 6.85 | 1.23 | 2.05 | 2.05 |

[1] The LOQ is 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA.
[2] HAFT = Highest-Average Field Trial.

*Conclusions*: The submitted field trials for mustard greens, the representative commodity of the *Brassica* leafy greens (subgroup 5B), reflect the proposed crop use pattern and are supported by acceptable storage stability data. Geographic representation of residue data for mustard greens is adequate. Samples were analyzed for diflubenzuron residues of concern using adequate data-collection methods. The submitted data for mustard greens were entered into the tolerance spreadsheet (see Appendix I). Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, HED recommends a tolerance level of 9.0 ppm for residues in/on *Brassica* leafy greens (subgroup 5B).

Turnip Greens

Turnip greens will be removed from Crop Group 2: Leaves of root and tuber vegetables group, and will become a member of Crop Subgroup 5B: Leafy *Brassica* greens (Reviewer's Guide and Summary..., B. Schneider, 6/14/02). Forage turnip varieties grown for livestock feed uses only will remain in Crop Group 2: Leaves of root and tuber vegetables group. As mustard greens are the representative commodity of the *Brassica* leafy greens (subgroup 5B), HED recommends a tolerance level of 9.0 ppm for residues in/on turnip greens. However, the label should be amended to prohibit use on dual purpose turnip cultivars or varieties which produce a harvestable

root.

Eggplant

No residue data were submitted in support of the proposed tolerance for eggplant. The petitioner requests translation of the available data from pepper to eggplant. However, HED does not generally translate residue data among members of a crop group unless a crop group tolerance is established.

*Conclusions*: The available data for peppers may not be translated to support the requested tolerance of 1.0 ppm for residues in/on eggplant. Thus, the proposed tolerance for eggplant should be withdrawn and the use directions for eggplant removed from the label until adequate eggplant residue data are available or a crop group tolerance for fruiting vegetables is established.

Okra

No residue data were submitted in support of the proposed tolerance for okra. The petitioner requests translation of the available pepper data to okra and has included in the administrative materials of the petition a technical proposal to amend the definition of fruiting vegetables (except cucurbits) to add okra. However, HED does not generally translate residue data among members of a crop group unless a crop group tolerance is established.

*Conclusions*: The available data for peppers may not be translated to support the requested tolerance of 1.0 ppm for residues in/on okra. Thus, the proposed tolerance for okra should be withdrawn and the use directions for okra removed from the label until adequate okra residue data are available or a crop group tolerance for fruiting vegetables is established.

Peanut

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Twelve peanut field trials were conducted in EPA Zones 2, 3, and 6 during the 2001 growing season. At each trial location, diflubenzuron (2 lb/gal FlC) was applied three times as broadcast foliar applications using ground equipment at 0.121-0.132 lb ai/A/application for a total rate of 0.373-0.385 lb ai/A (1x). The first application was at first bloom, the second was 14 (± 1) days after the first, and the third was 28 (± 1) days before harvest at nine sites, 20 days at two sites and 26 days at one site. A single control and single or duplicate treated samples of peanuts and peanut hay were harvested from each site at 20-28 DAT. Additional samples of peanut nutmeat and hay were collected from one site at 15, 20, 29, and 35 DAT to generate residue decline data. All samples were stored frozen for up to 481 days prior to residue extraction and analysis, an interval partially supported by available storage stability data.

The harvested samples were analyzed for residues of diflubenzuron using HPLC/UV method for nutmeat and hay, for residues of CPU using HPLC/MS/MS or UV for nutmeat or GC/MS methods for hay, and for residues of PCA using GC/MS method for nutmeat and hay. These methods, which are similar or based on method submissions previously deemed acceptable by HED, were adequately validated in conjunction with the field sample analyses.

The results from three field sites (Trial IDs TN03, GA01, and GA03) showed possible sample contamination since residues of diflubenzuron or CPU in/on control samples of peanut nutmeat were equal to or higher than treated samples. No adequate explanation was provided except a statement from the petitioner commenting that the magnitude of residues in/on control samples which bore quantifiable residues was low relative to the residues in/on treated samples.

When samples from Trial IDs TN03, GA01, and GA03 are excluded, the combined residues of diflubenzuron, CPU and PCA ranged <0.060-<0.070 ppm in/on 18 samples of peanut nutmeat and 1.12-18.46 ppm in/on 11 samples of peanut hay that were harvested 20-28 days following the last of three foliar treatments of a 2 lb/gal FlC test formulation for a total application rate of 0.373-0.385 lb ai/A; see Table 9. The HAFT values were <0.070 ppm for nutmeat and 18.46 ppm for hay. The average combined residues were 0.06 ppm for nutmeat and 7.14 ppm for hay.

The submitted residue decline data for peanut nutmeat is inconclusive, and a trend could not be established because residues of the parent and its metabolites were all below the respective LOQs from samples collected at PHIs of 15, 20, 29, and 35 days. Although detectable residues in peanut hay were observed from the decline trial, a meaningful trend in residue decline could not also be established since residue levels fluctuated at various sampling intervals.

**Table 9. Summary of Residue Data from Peanut Field Trials with Diflubenzuron.**

| Commodity | Total Applic. Rate(lb ai/A) | PHI (days) | Combined Residue Levels (ppm)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | n | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Nutmeat | 0.373-0.385 | 20-28 | 18 | <0.060 | <0.070 | <0.070 | 0.060 | 0.060 | 0.0 |
| Hay | | | 11 | 1.12 | 18.46 | 18.46 | 7.17 | 7.14 | 6.24 |

[1] The LOQ is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA in nutmeat.
[2] HAFT = Highest Average Field Trial.

*Conclusions*: The submitted field trials for peanuts reflect the proposed crop use pattern and are supported by acceptable storage stability data. However, geographic representation of residue data for is inadequate because the results from three trials were invalidated because of possible sample contamination. Confirmatory residue data from additional three peanut field trials conducted in Zone 2 are requested. Although geographic representation of data is incomplete, the residue values reported for peanut hay were entered into HED's tolerance spreadsheet. The residue values for peanut nutmeat were not entered into the tolerance spreadsheet because the combined residues ranged from <0.060 to <0.070 ppm. Based on the available data, HED tentatively recommends tolerance levels of 0.10 ppm for residues in/on peanut nutmeat and 55 ppm for residues in/on peanut hay.

### 860.1520 Processed Food and Feed

Peanut

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In a field trial conducted during the 2001 growing season in TX, diflubenzuron (2 lb/gal FlC) was applied to peanuts as three broadcast foliar applications during the crop's developmental stage at ~0.125 lb ai/A/application for a total rate of 0.379 lb ai/A (1x the field rate). Single bulk samples of untreated and treated peanuts were harvested at commercial maturity, 29 DAT. The

harvested peanuts were dried, shelled, and processed into meal and refined oil using simulated commercial practices. Prior to analysis, peanut nutmeat, meal, and oil were stored frozen for 244-639 days; the storage intervals are supported by the concurrent storage stability data.

The peanut nutmeat and its processed commodities (meal and refined oil) were analyzed for residues of diflubenzuron using an HPLC/UV method, for residues of CPU using an HPLC/MS/MS or UV method, and for residues of PCA using a GC/MS method. These methods, which are similar or based on method submissions previously deemed acceptable by HED, were adequately validated in conjunction with the peanut sample analyses.

The results (Table 10) show that combined residues of diflubenzuron, CPU, and PCA were below the combined method LOQ (<0.06 ppm) in/on peanut nutmeat treated at a seasonal rate of 0.379 lb ai/A. Following processing of the treated nutmeat, the combined residues were below the method LOQs (<0.525 ppm) in peanut meal and <0.066 ppm (below the LOQ for diflubenzuron and PCA, and 0.011 ppm for CPU) in peanut oil. Processing factors for meal and oil could not be reliably calculated due to differing LOQs and <LOQ residues in all matrices (raw and unprocessed). Table 1 of OPPTS 860.1520 reports that the maximum theoretical concentration factor (by crop) is 3x for peanuts.

**Table 10. Residue Data from Peanut Processing Study with Diflubenzuron.**

| RAC | Processed Commodity | Total Rate (lb ai/A) | PHI (days) | Diflubenzuron + CPU + PCA = Combined Residues (ppm) | Processing Factor (Combined Residues) |
|---|---|---|---|---|---|
| Peanut | Nutmeat (RAC) | 0.379 | 29 | <0.05 + <0.005 + <0.005 = <0.06 | -- |
| | Meal | | | <0.5 + <0.02 + <0.005 = <0.525 | NC[1] |
| | Refined oil | | | <0.05 + 0.011 + <0.005 = <0.066 | NC |

[1] Processing factors could not reliably be calculated (NC) because most residues were below the respective LOQ for that matrix.

*Conclusions*: The submitted peanut processing study is inadequate because the study has not definitively proven that diflubenzuron residues of concern will not concentrate in the processed commodities of peanuts as a result of the proposed use. In the current processing study, individual residues of diflubenzuron and its metabolites were each below the respective LOQs in/on treated peanut nutmeat. It is noted that higher individual and combined residues were reported for 1x-treated peanut nutmeat in HED review of the submitted field trial data. The petitioner is requested to conduct a new peanut processing study using a minimum seasonal rate of ≥3x, which is the maximum theoretical concentration factor (by crop) for peanuts. The meal samples from this study should be analyzed with a method which has a LOQ for diflubenzuron which is comparable to that of the RAC (0.05 ppm). Pending receipt of these data, HED concludes that the proposed tolerance of 0.2 ppm for residues in/on peanut oil is appropriate (HAFT residue (<0.06 ppm; see Table 9) multiplied by the maximum theoretical concentration factor of 3x).

Wheat

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In a field trial conducted during the 2002 growing season in WA, diflubenzuron (2 lb/gal FlC) was applied to a wheat crop (pre-booting growth stage) as one broadcast foliar application at rates of 0.066 or 0.646 lb ai/A (1x and 10x the field rate, respectively). Single bulk samples of control and treated wheat grain were harvested at commercial maturity, 83 DAT. Wheat grain

was processed into aspirated grain, germ, bran, flour, shorts and middlings using simulated commercial procedures.

Prior to analysis, wheat grain and processed products were stored frozen for up to 90-113 days, and one wheat germ sample was stored for up 321 days prior to analysis of diflubenzuron. The storage conditions and intervals of processed samples are marginally supported by storage stability data. The available storage stability data for rice bran may be translated to wheat bran; however, the petitioner is requested to generate storage stability data for wheat flour, middlings, shorts, and germ.

Samples of wheat grain and its processed commodities were analyzed for residues of diflubenzuron, CPU, and PCA, using HPLC/UV, GC/MS, and GC/MS with selected ion monitoring, respectively. These methods, which are similar or based on method submissions previously deemed acceptable by HED, were adequately validated in conjunction with the field sample analyses. The LLMV is 0.05 ppm for diflubenzuron and 0.005 ppm for CPU and PCA in all wheat matrices.

The results (Table 11) show that following one application of the test formulation at 0.066 lb ai/A (1x), individual residues of diflubenzuron, CPU, and PCA were each below the respective LOQ in/on the RAC (wheat grain) for a combined total of <0.06 ppm. The combined residues were <0.06 ppm in shorts, middlings, flour, bran, and germ, and were <2.104 ppm in aspirated grain fractions. These data indicate that the combined residues did not concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 1x-treated wheat grain is >35x.

Following one application of the test formulation at 0.646 lb ai/A (10x), individual residues of diflubenzuron, CPU, and PCA were 0.147 ppm, <0.005 ppm, and <0.005 ppm, respectively in/on the RAC (wheat grain) for a combined total of <0.157 ppm. The combined residues were <0.085 ppm in shorts, <0.06 ppm in middlings, <0.06 ppm in flour, <0.104 ppm in bran, <0.061 ppm in germ, and <28.069 ppm in aspirated grain fractions. These data also indicate that the combined residues did not concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 10x-treated wheat grain is 180x.

**Table 11. Residue Data from Wheat Processing Study with Diflubenzuron.**

| RAC | Processed Commodity | Total Rate (lb ai/A) | PHI (days) | Diflubenzuron + CPU + PCA = Combined Residues (ppm) | Processing Factor (Combined Residues) |
|---|---|---|---|---|---|
| Grain | RAC | 0.066 | 83 | <0.05 + <0.005 + <0.005 = <0.06 | -- |
| | Shorts | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Middlings | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Flour | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Bran | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Germ | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Aspirated grain | | | 2.094 + <0.005 + <0.005 = <2.104 | >35x |
| Grain | RAC | 0.646 | 83 | 0.147 + <0.005 + <0.005 = <0.157 | -- |
| | Shorts | | | 0.075 + <0.005 + <0.005 = <0.085 | 0.54x |
| | Middlings | | | <0.05 + <0.005 + <0.005 = <0.06 | 0.38x |
| | Flour | | | <0.05 + <0.005 + <0.005 = <0.06 | 0.38x |

| Table 11. Residue Data from Wheat Processing Study with Diflubenzuron. | | | | | |
|---|---|---|---|---|---|
| RAC | Processed Commodity | Total Rate (lb ai/A) | PHI (days) | Diflubenzuron + CPU + PCA = Combined Residues (ppm) | Processing Factor (Combined Residues) |
| | Bran | | | 0.094 + <0.005 + <0.005 = <0.104 | 0.66x |
| | Germ | | | 0.051 + <0.005 + <0.005 = <0.061 | 0.42x |
| | Aspirated grain | | | 27.920 + 0.144 + <0.005 = <28.069 | 180x |

*Conclusions*: The wheat processing study is acceptable pending submission of additional storage stability data. The combined residues of diflubenzuron and its CPU and PCA metabolites do not appear to concentrate in shorts, middlings, flour, bran, and germ processed from wheat grain treated at 1x and 10x the field rate. The combined residues, however, concentrated >35x and 180x in aspirated grain fractions processed from wheat grain treated at 1x and 10x, respectively.

The maximum diflubenzuron residues of concern expected in wheat aspirated grain fractions is 6.42 ppm which is derived by multiplying the HAFT residue (<0.06 ppm; see Table 7) with the processing factor generated from RAC samples with quantifiable residues (180x). Based on this calculation, HED recommends a tolerance for aspirated grain fractions at 11 ppm.

### 860.1650 Submittal of Analytical Reference Standards

Analytical standards for diflubenzuron and its metabolites CPU and PCA are currently available in the National Pesticide Standards Repository [6/16/2006 e-mail communication between D. Wright of ACB/BEAD and D. Martinez of Dynamac].

### 860.1850 Confined Accumulation in Rotational Crops

MRID 43274101 (DP# 205481, S. Knizner, 2/2/1995)

The nature of the residue in rotational crops is adequately understood for purposes of reregistration (Residue Chemistry Chapters for the RED document, 3/15/95). Although the available confined rotational crop study was inadequate to fully satisfy GLN 165-1 reregistration requirements, another confined rotational crop study will not be requested because the study allowed HED to make regulatory conclusions regarding the need for limited rotational-crop studies and to comment on the appropriateness of the currently established PBIs on diflubenzuron end-use product labels.

### 860.1900 Field Accumulation in Rotational Crops

MRID 44689703 (DP#s 244487, 251221, 251609, 253041, 253043; G. Kramer, 2/17/99)

An acceptable limited field rotational crop study has been submitted. HED review of the study concluded that quantifiable residues of diflubenzuron, CPU and PCA are unlikely to occur in rotated crops planted at least 30 days following application of diflubenzuron at an application rate of 0.375 lb ai/A to the primary crop given the low number of samples bearing residues of diflubenzuron or CPU and the low levels (0.01-0.06 ppm) of these residues. As the proposed application rates to primary annual crops are ≤0.375 lb ai/A, the proposed PBI of 30 days is appropriate.

## 860.1550 Proposed Tolerances

The HED MARC (DP# 272976, G. Kramer and G. Reddy, 5/31/2001) has determined that the residues of concern, for the purpose of tolerance expression, are diflubenzuron and its metabolites PCA and CPU. The proposed tolerance expression, listed in Section F of the petitions discussed herein, is in agreement with HED MARC's determination.

Tolerances for residues of diflubenzuron are established under 40 CFR §180.377. Tolerances listed in 40 CFR §180.377(a)(1) are expressed in terms of diflubenzuron *per se* whereas tolerances listed under in 40 CFR §180.377(a)(2) and 40 CFR §180.377(b) are expressed in terms of the combined residues of diflubenzuron and its metabolites CPU and PCA.

A summary of tolerance reassessment is presented in Table 12. The recommended tolerances for all commodities except barley grain, wheat grain, and peanut nutmeat were derived with the aid of HED's tolerance spreadsheet. The tolerance spreadsheet was not used for the above-listed commodities because residues in/on treated samples were mostly below the respective LOQs. The recommended tolerances for the commodities of small grains are contingent upon the requested label revisions to specify appropriate PHIs.

Codex Harmonization

The Codex Alimentarius has established maximum residue limits (MRL), expressed in terms of diflubenzuron *per se*, for many commodities including: apple (5 ppm), citrus fruits (0.5 ppm), edible offal (mammalian) (0.1 ppm), eggs (0.05 ppm), meat (from mammals other than marine mammals) (0.1 ppm), milks (0.02 ppm), mushrooms (0.3 ppm), pear (5 ppm), pome fruits (5 ppm), poultry meat (0.05 ppm), rice (0.01 ppm), and rice straw and fodder (dry) 0.7 ppm). As the U.S. residue definition includes CPU and PCA, compatibility is not possible with the proposed tolerances. A copy of the International Residue Limit Status (IRLS) sheet is attached to this memorandum.

**Table 12. Tolerance Summary for Diflubenzuron.**

| Commodity | Proposed Tolerance (ppm) | Recommended Tolerance (ppm) | Comments; *[Correct Commodity Definition]* |
|---|---|---|---|
| **Tolerances Proposed in PP#5E6965** | | | |
| Barley, grain | 0.06 | 0.06 | |
| Barley, forage | 5.0 | Delete | Not a RAC of barley as per Table 1 of OPPTS 860.1000. |
| Barley, hay | 2.0 | 3.0 | |
| Barley, straw | 2.0 | 1.8 | |
| Oat, grain | 0.06 | 0.06 | The available data for wheat may be translated to oat; the corresponding tolerances recommended for wheat commodities also apply to oat commodities. |
| Oat, forage | 5.0 | 7.0 | |
| Oat, hay | 2.0 | 6.0 | |
| Oat, straw | 2.0 | 3.5 | |
| Wheat, grain | 0.06 | 0.06 | |
| Wheat, forage | 5.0 | 7.0 | |

| Table 12. Tolerance Summary for Diflubenzuron. | | | |
|---|---|---|---|
| Commodity | Proposed Tolerance (ppm) | Recommended Tolerance (ppm) | Comments; *[Correct Commodity Definition]* |
| Wheat, hay | 2.0 | 6.0 | |
| Wheat, straw | 2.0 | 3.5 | |
| Grain, aspirated fractions | 3.0 | 11 | The maximum diflubenzuron residues of concern expected in wheat aspirated grain fractions is 6.42 ppm which is derived by multiplying the HAFT residue (<0.06 ppm; see Table 7) with the processing factor (180x). |
| Pummelo | 0.5 | 0.50 | The available data for citrus fruits may be translated to pummelo. |
| **Tolerances Proposed in PP#5E6966** | | | |
| *Brassica*, leafy greens, subgroup 5B | 8.0 | 9.0 | |
| Turnip greens | 8.0 | 9.0 | |
| Eggplant | 1.0 | Delete | Residue data for eggplant are required to determine appropriate tolerance. |
| Okra | 1.0 | Delete | Residue data for okra are required to determine appropriate tolerance. |
| **Tolerances Proposed in PP#5E6967** | | | |
| Peanut | 0.2 | 0.10 | |
| Peanut, hay | 20.0 | 55 | |
| Peanut, refined oil | 0.2 | 0.20 | *Peanut, oil*<br>A new peanut processing study is requested. |

## References

DP#: 261060
Subject: PP# 8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Results of Petition Method Validation (PMV). *Case 289260. Submission S571149.*
From: G. Kramer
To: R. Kumar and M. Laws
Dated: 9/6/2002
MRID(s): 443993-03 & -06

DP#: 272976
Subject: Health Effects Division (HED) Metabolism Assessment Review Committee (MARC) Meetings of 2/20/01 & 5/8/01. Diflubenzuron. Residues of Concern for Cancer Risk Assessment. Chemical 108201.
From: G. Kramer and G. Reddy
To: Y. Donovan
Dated: 5/31/2001
MRID(s): None

DP#: 272978
Subject: Diflubenzuron (Dimilin™ 2L, EPA Reg #400-461) in/on Pears. Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: S. Brothers and R. Forrest
Dated: 4/3/2001
MRID(s): 451196-01 and -02

DP#: 254273
Subject: Submission of Multiresidue Method (MRM) test information for updating PAM-I, Appendix II:
From: J. Rowell
To: B. McMahon
Dated: 3/22/199
MRID(s): 44707401

DP#: 254275
Subject: PP# 8F4925. Multiresidue Method Testing of p-Chloroaniline and 4-Chlorophenylurea in Rice Grain and Soybeans.
From: J. Rowell
To: F. Griffith
Dated: 3/22/1999
MRID(s): 44707401

DP#s: 253043, 253041, 244487, 251221 and 251609
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Amendments of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for Metabolites, Revised Label, Additional Residue, Storage Stability and Rotational Crop Data.
From: G. Kramer
To: M. Johnson/A. Sibold
Dated: 2/17/1999
MRIDs44577601, 44689701-02, 44699201, 44692701, 44692703, 4469500102, and 44707401

DP#: 240107
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Evaluation of Residue Data and Analytical Methods.
From: G. Kramer
To: T. Levine
Dated: 6/23/1998
MRID(s): 44486401, 44399301 thru 44399306

DP#: 209032
Subject: Chemistry Chapters of the Reregistration Eligibility Document
From: S. Knizner
To: S. Jennings, K, Whitby, and L. Kutney
Dated: 3/15/1995
MRID(s): None

DP#s: 205481
Subject: Diflubenzuron. Confined Rotational Crop Study.
From: S. Knizner
To: S. Jennings
Dated: 2/1/1995
MRID(s): 43274101

Attachments:
IRLS sheet
Appendix I - Tolerance Assessment Calculations

cc: G. Kramer (RAB1)
RDI: P.V. Shah (8/30/06); RAB1 Chemists (8/30/06)
G.F. Kramer:S10781:PY-S:(703)305-5079:7509P:RAB1

Template Version September 2005

# INTERNATIONAL RESIDUE LIMIT STATUS

| Chemical Name: *N*-[[(4-chlorophenyl) amino]carbonyl]-2,6-difluorobenzamide | Common Name: Diflubenzuron | X Proposed tolerance<br>X Reevaluated tolerance<br>☐ Other | Date: 06/23/2006 |
|---|---|---|---|

| Codex Status (Maximum Residue Limits) | Proposed U. S. Tolerances |
|---|---|
| ☐ No Codex proposal step 6 or above<br>☐ No Codex proposal step 6 or above for the crops requested | Petition Number: PP#5E6965, PP#5E6966, and PP#5E6967<br>DP#s: 321623, 321625, and 321627 |
| Residue definition (step 8/CXL): Diflubenzuron *per se* | Reviewer/Branch: RAB1 |
| | Residue definition: Combined residues of diflubenzuron and its metabolites PCA and CPU |

| Crop (s) | MRL (mg/kg) | Crop(s) | Tolerance (ppm) |
|---|---|---|---|
| Apple | 5 | Barley, grain | 0.06 |
| Citrus fruits | 0.5 | Oat, grain | 0.06 |
| Edible offal (mammalian) | 0.1 | Wheat, grain | 0.06 |
| Eggs | 0.05 | Barley, forage | 5.0 |
| Meat (from mammals other than marine mammals) | 0.1 | Oat, forage | 5.0 |
| Milks | 0.02 | Wheat, forage | 5.0 |
| Mushrooms | 0.3 | Barley, hay | 2.0 |
| Pear | 5 | Oat, hay | 2.0 |
| Pome fruits | 5 | Wheat, hay | 2.0 |
| Poultry meat | 0.05 | Barley, straw | 2.0 |
| Rice | 0.01 | Oat, straw | 2.0 |
| Rice straw and fodder, Dry | 0.7 | Wheat, straw | 2.0 |
| | | Grain, aspirated fractions | 3 |
| | | Pummelo | 0.5 |
| | | Peanut | 0.2 |
| | | Peanut, hay | 20 |
| | | Peanut, refined oil | 0.2 |
| | | *Brassica*, leafy greens, (subgroup5B) | 8.0 |
| | | Turnip greens | 8.0 |
| | | Eggplant | 1.0 |
| | | Okra | 1.0 |

| Limits for Canada | Limits for Mexico |
|---|---|
| X No Limits<br>☐ No Limits for the crops requested | ☐ No Limits<br>☐ No Limits for the crops requested |
| Residue definition: | Residue definition: |

| Crop(s) | MRL (mg/kg) | Crop(s) | MRL (mg/kg) |
|---|---|---|---|

Rev. 1998

## APPENDIX I. Tolerance Assessment Calculations.

The Agency's *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* was utilized for determining appropriate tolerance levels for: mustard greens, peanut hay, barley hay, barley straw, wheat forage, wheat hay, and wheat straw. The combined residue levels of diflubenzuron in these commodities were readily quantifiable, and in each case, <10% of the residue values were below the LOQ. Residue data for peanut nutmeat, barley grain, and wheat grain were not entered into the spreadsheet because >15% of residue values were below the LOQ.

The dataset used to establish a tolerance for combined diflubenzuron residues on mustard greens consisted of field trial data representing application rates of 0.19-0.26 lb ai/A (3 or 4 applications at 0.061-0.066 lb ai/A/application) with a 6- to 8-day PHI. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs are within 25% of the maximum label application rate and minimum label PHI, respectively. The residues values used to calculate the tolerance are provided in Table I-1.

The dataset used to establish a tolerance for combined diflubenzuron residues on peanut hay consisted of field trial data representing application rates of 0.373-0.385 lb ai/A (3 applications at 0.121-0.132 lb ai/A/application) with a 20- to 28-day PHI. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs are within 25% of the maximum label application rate and minimum label PHI, respectively. The residues values used to calculate the tolerance are provided in Table I-2.

The dataset used to establish tolerances for combined diflubenzuron residues on barley hay and straw consisted of field trial data representing application rates of 0.0592-0.0629 lb ai/A with a 15- to 39-day PHI for hay and a 50- to 76-day PHI for straw. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs are within 25% of the maximum label application rate and minimum label PHI, respectively. The residues values used to calculate the tolerances are provided in Table I-3.

The dataset used to establish tolerances for combined diflubenzuron residues on wheat forage, hay, and straw consisted of field trial data representing application rates of 0.0619-0.0642 lb ai/A with a 3- to 12-day PHI for forage, a 28- to 32-day PHI for hay, and a 56- to 62-day PHI for straw. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates and PHIs are within 25% of the maximum label application rate and minimum label PHI, respectively. The residues values used to calculate the tolerances are provided in Table I-4.

For peanut hay, barley hay, barley straw, wheat forage, wheat hay, and wheat straw, visual inspection of the lognormal probability plots (Figures 3, 5, 7, 9, 11, and 13) indicates that the datasets are reasonably lognormal, and the result from the approximate Shapiro-Francia test statistic (Figures 4, 6, 8, 10, 12, and 14) confirmed that the assumption of lognormality should not be rejected. For mustard greens, visual inspection of the lognormal probability plot and the result from the approximate Shapiro-Francia test statistic indicate that the dataset for mustard greens is not lognormal.

Since the field trial data for diflubenzuron on mustard greens are not lognormal, the upper bound on the 89$^{th}$ percentile should be selected as the tolerance value (distribution-free method). Using

the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the upper bound on the 89$^{th}$ percentile rounds to the value 9.0 ppm. Therefore, 9.0 ppm is the recommended tolerance level for diflubenzuron on mustard greens.

Since the field trial data for diflubenzuron on peanut hay represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% upper confidence limit (UCL) on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 55 ppm is the recommended tolerance level for diflubenzuron on peanut hay.

Since the field trial data for diflubenzuron on barley hay represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% UCL on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 3.0 ppm is the recommended tolerance level for diflubenzuron on barley hay.

Since the field trial data for diflubenzuron on barley straw represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% UCL on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 1.8 ppm is the recommended tolerance level for diflubenzuron on barley straw.

Since the field trial data for diflubenzuron on wheat forage represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% UCL on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 7.0 ppm is the recommended tolerance level for diflubenzuron on wheat forage.

Since the field trial data for diflubenzuron on wheat hay represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% UCL on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 6.0 ppm is the recommended tolerance level for diflubenzuron on wheat hay.

Since the field trial data for diflubenzuron on wheat straw represent a small dataset (i.e., less than 15 samples) and are reasonably lognormal, the upper bound estimate of the 95th percentile based on the median residue value was compared to the minimum of the 95% UCL on the 95th percentile and the point estimate of the 99th percentile, and the minimum value was selected as

the tolerance value. Using the rounding procedure as outlined in the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data SOP*, 3.5 ppm is the recommended tolerance level for diflubenzuron on wheat straw.

| **Table I-1. Residue data used to calculate tolerance for diflubenzuron on mustard greens.** | |
|---|---|
| **Regulator:** | EPA |
| **Chemical:** | Diflubenzuron |
| **Crop:** | Mustard greens |
| **PHI:** | 6-8 Days |
| **App. Rate:** | 0.190-0.256 lb ai/A |
| **Submitter:** | IR-4 |
| **MRID Citation:** | MRID 46609601 |
| | **Combined Residues of Diflubenzuron (ppm)** |
| | 1.04 |
| | 1.18 |
| | 0.84 |
| | 2.21 |
| | 1.97 |
| | 3.09 |
| | 1.10 |
| | 0.93 |
| | <0.065 |
| | <0.065 |
| | 1.19 |
| | 1.26 |
| | 1.28 |
| | 2.91 |
| | 7.07 |
| | 6.62 |

**Figure 1: Lognormal Probability Plot of Combined Diflubenzuron Residues in Mustard Greens.**

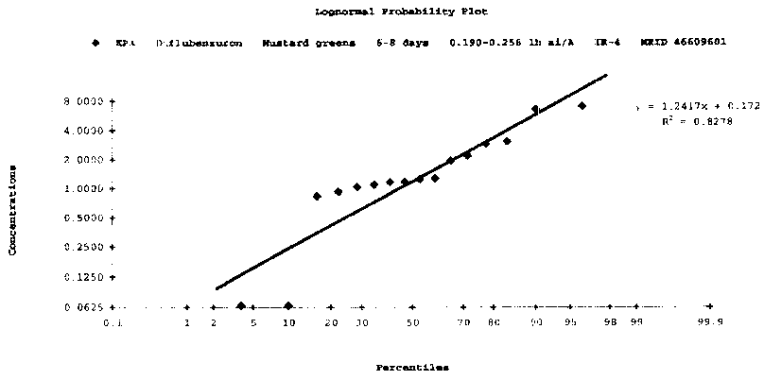


**Figure 2: Data summary table for combined residues of diflubenzuron in mustard greens.**

| | | | |
|---|---|---|---|
| | **Regulator:** | EPA | |
| | **Chemical:** | Diflubenzuron | |
| | **Crop:** | Mustard greens | |
| | **PHI:** | 6-8 days | |
| | **App. Rate:** | 0.190-0.256 lb ai/A | |
| | **Submitter:** | IR-4 | |
| | **MRID Citation:** | MRID 46609601 | |
| | **n:** | 16 | |
| | **min:** | 0.07 | |
| | **max:** | 7.07 | |
| | **median:** | 1.23 | |
| | **average:** | 2.05 | |
| | **95th Percentile** | **99th Percentile** | **99.9th Percentile** |
| **EU Method I Normal** | 6.0 (8.0) | 7.0 (10) | 9.0 (--) |
| **EU Method I Log Normal** | 11 **(35)** | **25** (110) | 70 (--) |
| **EU Method II Distribution-Free** | | 6.0 | |
| **California Method μ+ 3σ** | | 9.0 | |
| **UPLMedian95th** | | **9.0** | |
| **Approximate Shapiro-Francia Normality Test** | | 0.8278 p-value <= 0.01: Reject lognormality assumption | |

Would you like the above values rounded? (Y or N)==> Y

| **Table I-2. Residue data used to calculate tolerance for diflubenzuron on peanut hay.** | |
|---|---|
| **Regulator:** | EPA |
| **Chemical:** | Diflubenzuron |
| **Crop:** | Peanut hay |
| **PHI:** | 20-28 Days |
| **App. Rate:** | 0.373-0.385 lb ai/A |
| **Submitter:** | IR-4 |
| **MRID Citation:** | MRID 46609401 |
| | **Combined Residues of Diflubenzuron (ppm)** |
| | 18.46 |
| | 10.79 |
| | 17.04 |
| | 8.42 |
| | 7.90 |
| | 2.70 |
| | 1.12 |
| | 1.18 |
| | 1.67 |
| | 7.17 |
| | 2.05 |

**Figure 3: Lognormal probability plot for combined residues of diflubenzuron in peanut hay.**

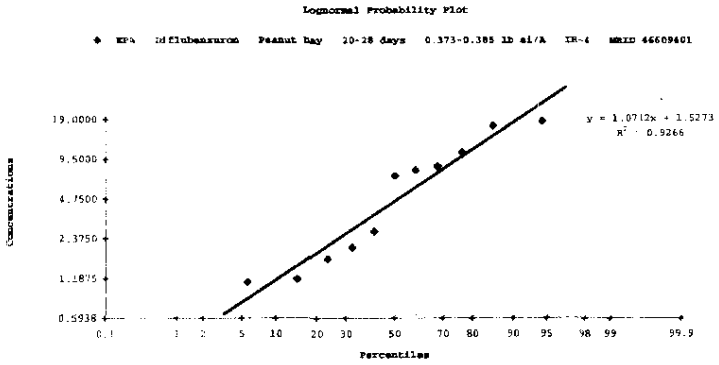



**Figure 4: Data summary table for residues of diflubenzuron in peanut hay.**

| | |
|---|---|
| **Regulator:** | EPA |
| **Chemical:** | Diflubenzuron |
| **Crop:** | Peanut hay |
| **PHI:** | 20-28 days |
| **App. Rate:** | 0.373-0.385 lb ai/A |
| **Submitter:** | IR-4 |
| **MRID Citation:** | MRID 46609401 |
| **n:** | 11 |
| **min:** | 1.12 |
| **max:** | 18.46 |
| **median:** | 7.17 |
| **average:** | 7.14 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| **EU Method I Normal** | 18 (25) | 25 (35) | 30 (--) |
| **EU Method I Log Normal** | 30 (90) | 90 (270) | 120 (--) |
| **EU Method II Distribution-Free** | 25 | | |
| **California Method μ+ 3σ** | 30 | | |
| **UPLMedian95th** | 35 | | |
| **Approximate Shapiro-Francia Normality Test** | 0.9266 p-value > 0.05 : Do not reject lognormality assumption | | |

Would you like the above values rounded? (Y or N)==> Y

| **Table I-3.** | **Residue data used to calculate tolerance for diflubenzuron on barley.** | |
|---|---|---|
| **Regulator:** | EPA | |
| **Chemical:** | Diflubenzuron | |
| **Crop:** | Barley Hay | Barley Straw |
| **PHI:** | 15-39 days | 50-76 days |
| **App. Rate:** | 0.0592-0.0629 lb ai/A | |
| **Submitter:** | IR-4 | |
| ***MRID Citation:*** | *MRID 46609501* | |
| | **Combined Residues of Diflubenzuron (ppm)** | **Combined Residues of Diflubenzuron (ppm)** |
| | 0.74 | 0.23 |
| | 0.76 | 0.15 |
| | 0.47 | 0.11 |
| | 0.82 | 0.14 |
| | 0.28 | 0.31 |
| | 0.70 | 0.32 |
| | 0.54 | 0.45 |

| Table I-3. Residue data used to calculate tolerance for diflubenzuron on barley. | | |
|---|---|---|
| | 0.66 | 0.48 |
| | 0.56 | 0.58 |
| | 0.73 | 0.56 |
| | 0.13 | <0.06 |
| | 0.13 | <0.06 |
| | 1.33 | 0.55 |
| | 1.47 | 0.56 |

**Figure 5: Lognormal probability plot of combined diflubenzuron residues in barley hay**

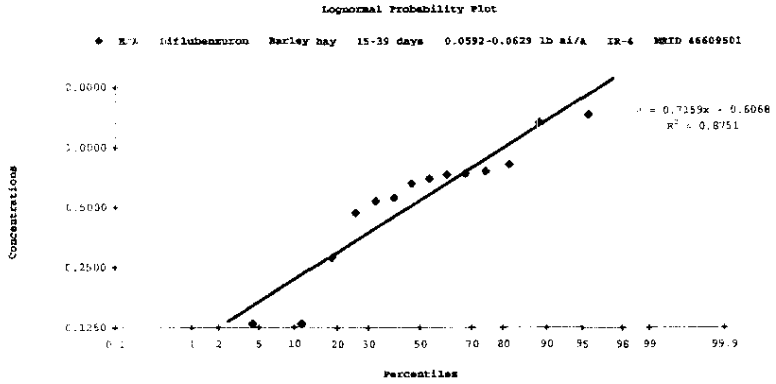



**Figure 6: Data summary table for combined residues of diflubenzuron in barley hay.**

| | | | |
|---|---|---|---|
| | **Regulator:** EPA | | |
| | **Chemical:** Diflubenzuron | | |
| | **Crop:** Barley hay | | |
| | **PHI:** 15-39 days | | |
| | **App. Rate:** 0.0592-0.0629 lb ai/A | | |
| | **Submitter:** IR-4 | | |
| | **MRID Citation:** MRID 46609501 | | |
| | **n:** 14 | | |
| | **min:** 0.13 | | |
| | **max:** 1.47 | | |
| | **median:** 0.68 | | |
| | **average:** 0.67 | | |
| | **95th Percentile** | **99th Percentile** | **99.9th Percentile** |
| **EU Method I Normal** | 1.3 (1.7) | 1.8 (2.5) | 1.9 (--) |
| **EU Method I Log Normal** | 1.9 **(4.0)** | 3.6 (8.0) | 6.0 (--) |
| **EU Method II Distribution-Free** | | 1.6 | |
| **California Method μ+ 3σ** | | **1.9** | |
| **UPLMedian95th** | | **5.0** | |
| **Approximate Shapiro-Francia Normality Test** | 0.8751 p-value > 0.05 : Do not reject lognormality assumption | | |

Would you like the above values rounded? (Y or N ==> Y

**Figure 7: Lognormal probability plot for combined residues of diflubenzuron in barley straw.**

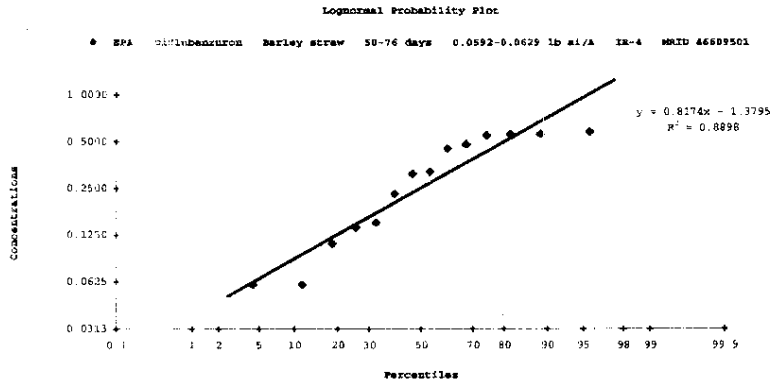



**Figure 8: Data summary table for combined residues of diflubenzuron in barley straw.**

| | |
|---|---|
| **Regulator:** | EPA |
| **Chemical:** | Diflubenzuron |
| **Crop:** | Barley straw |
| **PHI:** | 50-76 days |
| **App. Rate:** | 0.0592-0.0629 lb ai/A |
| **Submitter:** | IR-4 |
| **MRID Citation:** | MRID 46609501 |
| **n:** | 14 |
| **min:** | 0.06 |
| **max:** | 0.58 |
| **median:** | 0.32 |
| **average:** | 0.33 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| **EU Method I Normal** | 0.70 (0.90) | 0.80 (1.1) | 1.0 (--) |
| **EU Method I Log Normal** | 1.0 **(2.5)** | 3.0 (5.0) | 3.5 (--) |
| **EU Method II Distribution-Free** | 1.2 | | |
| **California Method μ+ 3σ** | **1.0** | | |
| **UPLMedian95th** | **2.5** | | |
| **Approximate Shapiro-Francia Normality Test** | 0.8898 p-value > 0.05 : Do not reject lognormality assumption | | |

Would you like the above values rounded? (Y or N) ==> Y

| **Table I-3. Residue data used to calculate tolerance for diflubenzuron on wheat.** | | | |
|---|---|---|---|
| **Regulator:** | EPA | | |
| **Chemical:** | Diflubenzuron | | |
| **Crop:** | Wheat Forage | Wheat Hay | Wheat Straw |
| **PHI:** | 3-12 days | 28-32 days | 50-76 days |
| **App. Rate:** | 0.0619-0.0642 lb ai/A | | |
| **Submitter:** | IR-4 | | |
| **MRID Citation:** | MRID 46609501 | | |
| | 1.17 | 0.90 | 0.24 |
| | 2.49 | 0.87 | 0.35 |
| | 2.65 | 1.25 | 0.78 |
| | 2.30 | 1.31 | 1.04 |
| | 3.97 | 0.26 | <0.06 |
| | 3.62 | 0.11 | 0.08 |

**Figure 9: Lognormal probability plot for combined residues of diflubenzuron in wheat forage.**

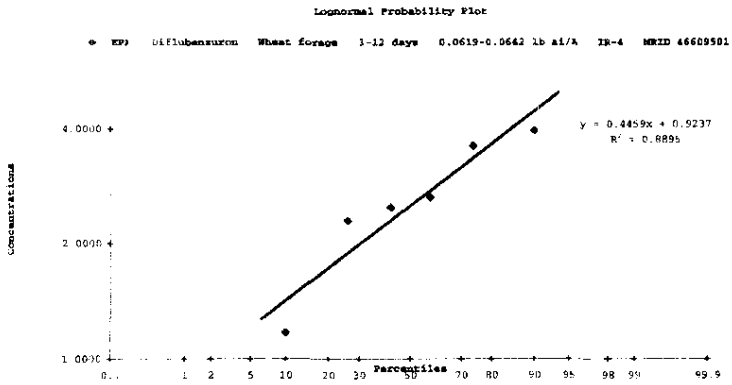



**Figure 10: Summary data for combined residues of diflubenzuron in wheat forage.**

| | | | |
|---|---|---|---|
| | Regulator: EPA<br>Chemical: Diflubenzuron<br>Crop: Wheat forage<br>PHI: 3-12 days<br>App. Rate: 0.0619-0.0642 lb ai/A<br>Submitter: IR-4<br>MRID Citation: MRID 46609501<br><br>n: 6<br>min: 1.17<br>max: 3.97<br>median: 2.57<br>average: 2.70 | | |
| | **95th Percentile** | **99th Percentile** | **99.9th Percentile** |
| **EU Method I Normal** | 4.5<br>(7.0) | 6.0<br>(8.0) | 6.0<br>(--) |
| **EU Method I Log Normal** | 6.0<br>**(13)** | [redacted]<br>(25) | 10<br>(--) |
| **EU Method II Distribution-Free** | 8.0 | | |
| **California Method μ+ 3σ** | **6.0** | | |
| **UPLMedian95th** | **30** | | |
| **Approximate Shapiro-Francia Normality Test** | 0.8895<br>p-value > 0.05 : Do not reject lognormality assumption | | |

Would you like the above values rounded? (Y or N) --> Y

**Figure 11: Lognormal probability plot of combined residues of diflubenzuron in wheat hay.**

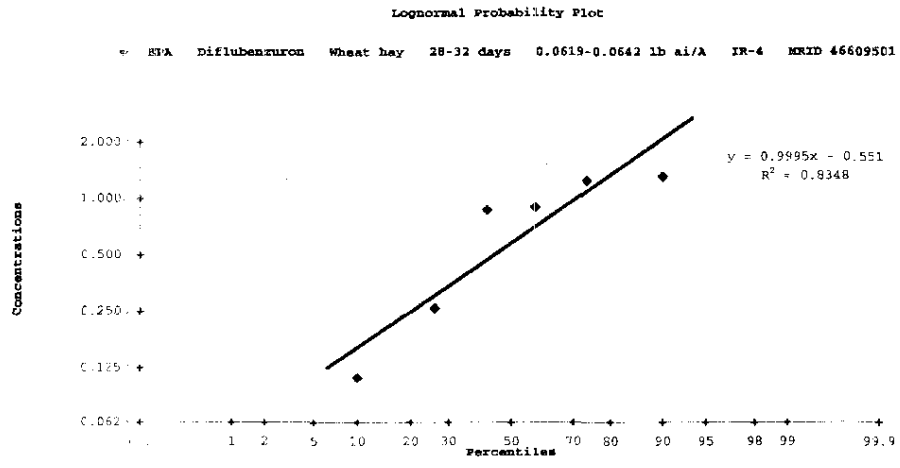


**Figure 12: Summary data of combined residues of diflubenzuron in wheat hay.**

| | |
|---|---|
| Regulator: | EPA |
| Chemical: | Diflubenzuron |
| Crop: | Wheat hay |
| PHI: | 28-32 days |
| App. Rate: | 0.0619-0.0642 lb ai/A |
| Submitter: | IR-4 |
| MRID Citation: | MRID 46609501 |
| n: | 6 |
| min: | 0.11 |
| max: | 1.31 |
| median: | 0.89 |
| average: | 0.78 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| EU Method I Normal | 1.7 (3.0) | 2.0 (3.5) | 2.5 (--) |
| EU Method I Log Normal | 3.0 (25) | 5.0 (95) | 13 (--) |
| EU Method II Distribution-Free | | 3.0 | |
| California Method μ+ 3σ | | 2.5 | |
| UPLMedian95th | | 11 | |
| Approximate Shapiro-Francia Normality Test | | 0.8348 p-value > 0.05 : Do not reject lognormality assumption | |

Would you like the above values rounded? (Y or N) Y

**Figure 13: Lognormal probability plot of combined residues of diflubenzuron in wheat straw.**

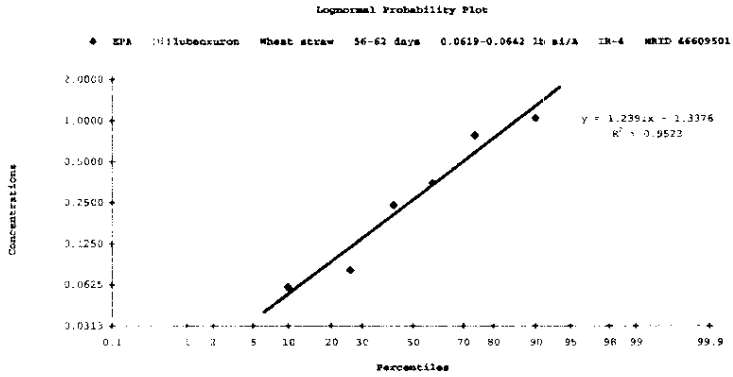



**Figure 14: Data summary for combined residues of diflubenzuron in wheat straw.**

| | |
|---|---|
| Regulator: | EPA |
| Chemical: | Diflubenzuron |
| Crop: | Wheat straw |
| PHI: | 56-62 days |
| App. Rate: | 0.0619-0.0642 lb ai/A |
| Submitter: | IR-4 |
| MRID Citation: | MRID 46609501 |
| n: | 6 |
| min: | 0.06 |
| max: | 1.04 |
| median: | 0.30 |
| average: | 0.43 |

| | 95th Percentile | 99th Percentile | 99.9th Percentile |
|---|---|---|---|
| EU Method I Normal | 1.1 (2.0) | 1.4 (2.5) | 1.7 (--) |
| EU Method I Log Normal | 1.8 (20) | 4.0 (95) | 10 (--) |
| EU Method II Distribution-Free | | 1.7 | |
| California Method μ+ 3σ | | 1.7 | |
| UPLMedian95th | | [illegible] | |
| Approximate Shapiro-Francia Normality Test | | 0.9523 p-value > 0.05 : Do not reject lognormality assumption | |

Would you like the above values rounded? (Y or N) Y

Primary Evaluator — Date: 14-SEP-2006
George F. Kramer, Ph.D., Senior Chemist
Registration Action Branch (RAB1)
Health Effects Division (HED) (7509P)

Approved by — Date: 14-SEP-2006
P.V. Shah, Ph.D. Branch Senior Scientist
RAB1/HED (7509P)

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Durham, NC 27713; submitted 06/23/2006). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## STUDY REPORT:

46609601. Samoil, K.S. (2004) Diflubenzuron: Magnitude of the Residue on Mustard Greens. Lab Project Number: 08031.01-PTR01. Unpublished study prepared by IR-4. 299 p.

## EXECUTIVE SUMMARY:

Eight field trials on mustard greens were conducted in EPA Zones 2, 3, 5, 6, and 10 during the 2001 growing season. At each location, diflubenzuron (2 lb/gal flowable concentrate (FlC)) was applied four times (except for one trial site where only three treatments were made) as broadcast foliar applications using ground equipment at 0.061-0.066 lb ai/A/application for a total rate of 0.19-0.26 lb ai/A. Treatments were made during the crop's vegetative growth stage at a retreatment interval of 8-15 days. Duplicate control and treated samples of mature mustard greens were harvested from each site at 6-8 days after treatment (DAT). Mustard green samples were stored frozen up to 520 days prior to residue analysis, an interval partially supported by available storage stability data.

The harvested samples of mustard greens were analyzed for residues of diflubenzuron, 4-chlorophenylurea (CPU), and 4-chloroaniline (PCA) using high-performance liquid chromatography (HPLC)/ultraviolet (UV), gas chromatography/electron-capture detection (GC/ECD) and GC/mass-selective detector (GC/MSD) methods, respectively. These methods, which are similar or based on method submissions previously deemed acceptable by the Agency, were adequately validated in conjunction with the field sample analyses. The limits of quantitation (LOQs) are 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA.

The results show that the combined residues of diflubenzuron, CPU, and PCA were <0.065 ppm-7.07 ppm in/on mustard greens harvested 6-8 days following the last of 3 to 4 foliar treatments of a 2 lb/gal FlC test formulation for a total application rate of 0.19-0.26 lb ai/A. The highest-average field trial (HAFT) was 6.85 ppm and the average combined residues were 2.05 ppm. No residue decline data were submitted.

## STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the mustard green field trial residue data are classified as acceptable and satisfy the guideline requirement for crop field trials (Residue Chemistry Guideline OPPTS 860.1500). The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 321623.

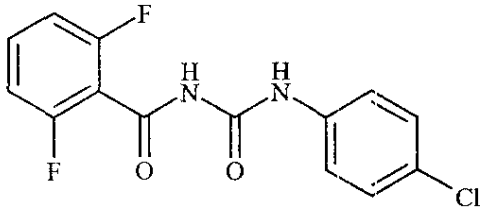
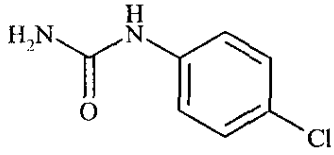
## COMPLIANCE:

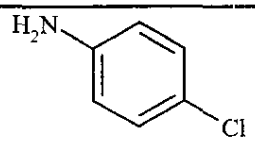
Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations were reported that would substantially impact the validity of the study.

## A. BACKGROUND INFORMATION

Diflubenzuron is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The Reregistration Eligibility Decision (RED) for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008). Tolerances for residues of diflubenzuron are established under 40 CFR §180.377.

**TABLE A.1. Diflubenzuron Nomenclature.**

| | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | Dimilin, Vigilante, Micromite, Adept |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Product (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461) |
| Regulated Metabolite |  |
| Common name | 4-chlorophenylurea (CPU) |

| TABLE A.1. Diflubenzuron Nomenclature. | |
|---|---|
| Regulated Metabolite |  |
| Common Name | 4-chloroaniline (PCA) |

| TABLE A.2. Physicochemical Properties of Diflubenzuron. | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | Not available | |
| Density | Not available | |
| Water solubility (25 °C) | 0.08 ppm | |
| Solvent solubility (25 °C) (ppm) | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25 °C) | $1.2 \times 10^{-4}$ mPa | |
| Dissociation constant, $pK_a$ | Not available | |
| Octanol/water partition coefficient, $Log(K_{OW})$ | 3.89 | |
| UV/visible absorption spectrum | Not available | |

## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Mustard greens were grown and maintained at each trial site (Table B.1.1) using typical agricultural practices for the respective geographical region. Soil conditions, temperature and precipitation as well as irrigation and weather conditions were within normal conditions for the region. Information was also provided on maintenance chemicals and other pesticides used at each site.

| TABLE B.1.1. Trial Site Conditions. | | | | |
|---|---|---|---|---|
| Trial Identification (City, State; Year) | Soil characteristics[1] | | | |
| | Type | %OM | pH | CEC (meq/g) |
| Weslaco, TX; 2001 | Sandy Clay | Not applicable; the use pattern tested in the study included on foliar applications. | | |
| Tifton, GA; 2001 | Sand | | | |
| Tifton, GA; 2001 | Sand | | | |
| Salinas, CA; 2001 | Loam | | | |
| Salinas, CA; 2001 | Sandy Loam | | | |
| Celeryville, OH; 2001 | Sandy Loam | | | |
| Crossville, TN; 2001 | Sandy Loam | | | |
| Gainesville, FL; 2001 | Sand | | | |

[1] OM = Organic matter, Cation-exchange capacity

**TABLE B.1.2. Study Use Pattern on Mustard Greens.**

| Location City, State; Year: Trial ID | EP[1] | Application | | | | | Tank Mix/ Adjuvants |
|---|---|---|---|---|---|---|---|
| | | Method; Timing | Volume GPA | Single Rate (lb ai/A) | RTI[2] (days) | Total Rate (lb ai/A) | |
| Weslaco, TX; 2001; TX27 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 30-42 | 0.063-0.065 | 8-12 | 0.256 | None |
| Tifton, GA; 2001; GA20 | 2 lb/gal FlC | Three broadcast foliar during vegetation [3] | 20 | 0.063-0.064 | 8-12 | 0.190 | None |
| Tifton, GA; 2001; GA21 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 20 | 0.063-0.064 | 12-15 | 0.254 | None |
| Salinas, CA; 2001; CA76 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 70-90 | 0.063-0.066 | 8-12 | 0.258 | None |
| Salinas, CA; 2001; CA77 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 34-74 | 0.061-0.65 | 8-12 | 0.253 | None |
| Celeryville, OH; 2001; OH19 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 50-51 | 0.063-0.065 | 8-12 | 0.255 | None |
| Crossville, TN; 2001; TN11 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 23-24 | 0.061-0.064 | 8-12 | 0.249 | None |
| Gainesville, FL; 2001; FL37 | 2 lb/gal FlC | Four broadcast foliar during vegetation | 30 | 0.063-0.064 | 10-15 | 0.254 | None |

[1] EP = End-use product; DIMILIN® 2L
[2] RTI = Retreatment interval.
[3] The crop was harvested early as plants were declining.

**TABLE B.1.3. Trial Numbers and Geographical Locations.**

| NAFTA Growing Zones[1] | *Brassica* Leafy Green (Subgroup 5-B) | | |
|---|---|---|---|
| | Submitted | Requested | |
| | | Canada | U.S. |
| 1 | --- | --- | -- |
| 2 | 3[2] | --- | 2 |
| 3 | 1 | --- | 1 |
| 4 | --- | --- | 1 |
| 5 | 1 | --- | 1 |
| 6 | 1 | --- | 1 |
| 7 | -- | --- | -- |
| 8 | -- | --- | -- |
| 9 | -- | --- | -- |
| 10 | 2 | --- | 2 |
| 11 | -- | --- | -- |
| 12 | -- | --- | -- |
| Total | 8 | NA | 8 |

[1] Zones 13-21 and 1A, 5A, 5B, and 7A were not included as the proposed use is for US only.
[2] No site was located within Zone 4; however, a Zone 2 trial was on the border of Zone 4.

## B.2. Sample Handling and Preparation

Duplicate control and treated samples of mustard greens (4-6 lbs) were harvested from each trial site at commercial maturity 6-8 days after the final application of the test formulation. All samples were placed in frozen storage within 2.75 hours of collection. Field storage time was not documented. Samples were shipped frozen by ACDS freezer truck to the analytical laboratory (PTRL West, Hercules, CA) where samples were stored at <0 °C until extraction for analysis.

## B.3. Analytical Methodology

Samples were analyzed for diflubenzuron using an HPLC/UV method as described in *High Performance Liquid Chromatographic Determination of Diflubenzuron Residues in Pecan Nuts, Method LAI 3-86-13, March 18, 1998.* Briefly, residues are extracted twice with ethyl acetate and filtered. Residues are evaporated to dryness and redissolved in hexane. Residues are partitioned with acetonitrile and again evaporated to dryness. Residues are redissolved with dichloromethane, and cleaned up on a Florisil solid-phase extraction (SPE) column. After clean up, residues are analyzed by HPLC on a C18 column with UV detection. The LOQ is 0.05 ppm; the limit of detection (LOD) was not reported.

Samples were analyzed for CPU using a GC/ECD method described in *Dimilin 25W Rotational Crop Study: Dimilin 25W Treated Cotton Rotated with Wheat, Lettuce, and Turnips 30, 45, 60, 120, 180, and 365 Days After Harvest, PTRL Study No. 614W, August 21, 1998.* Briefly, samples are dried with sodium sulfate and residues are extracted with ethyl acetate. Residues are evaporated to dryness, redissolved in acetone and petroleum ether, and cleaned up on a silica-gel SPE column. Again, residues are evaporated to dryness and redissolved in acetonitrile. The sample is filtered and derivatized in a glass tube with heptafluorobutyric anhydride for 10 minutes. Residues are then analyzed by GC/ECD. The LOQ is 0.01 ppm; the LOD was not reported.

Samples were analyzed for PCA using a GC/MSD method based on *Method Validation for 4-Chloroaniline (PCA) at Low Levels Using $^{13}$C-PCA as Internal Standard in Rice and Rice Commodities, PTRL Study No. 645W, February 2, 1998.* Briefly, residues are acidified with HCl and sonicated for 30 minutes at 60 °C. NaOH and NaCl are added, and residues are extracted three times with hexane. Residues are then partitioned with 0.1 N HCl, neutralized and extracted with hexane. Extracts are dried and cleaned up with a Florisil column, derivatized with heptafluorobutyric acid for 10 minutes, after which water, sodium carbonate and hexane are added. Residues in the hexane layer are analyzed by GC/MSD. The LOQ is 0.005 ppm, the LOD was estimated at 0.002 ppm.

In conjunction with the analysis of field trial samples, the above methods were validated using control samples of mustard greens fortified with diflubenzuron, CPU or PCA at 0.01-5.00 ppm.

## C. RESULTS AND DISCUSSION

The number and geographic locations of the mustard green field trials is adequate for the purpose of establishing a tolerance on *Brassica* Leafy Green (Subgroup 5-B). In seven mustard green field trials conducted during the 2001 growing season, diflubenzuron was applied four times to fields as broadcast foliar applications at 0.061-0.066 lb ai/A/application during crop development. Only three treatments were made at one trial (Trial ID GA 20; Tifton, GA) because the test crop was declining in vegetative vigor. A single control and duplicate treated samples of mature mustard greens were harvested from each site at 6-8 DAT.

The HPLC/UV, GC/ECD and GC/MSD methods used to determine residues of diflubenzuron, CPU, and PCA in/on mustard greens were adequately validated in conjunction with the field sample analyses. Method recoveries from concurrent analysis of samples as well as from additional method verification (see Table C.1) are well within the acceptable range of 70-120% except for two samples which reported diflubenzuron recoveries of 66% and 67%. The petitioner provided examples of residue calculation from the analytical phase of the study. No interference was observed in the regions of diflubenzuron, CPU, and PCA in chromatograms for control samples of mustard greens.

Samples of mustard greens were stored frozen up to 520 days prior to residue extraction and analysis (Table C.2.1). To validate sample storage conditions and intervals, a storage stability study was conducted as part of the residue field study. The results of this study (Table C.2.2) show that residues of diflubenzuron are reasonably stable in frozen mustard greens (average corrected stored recovery of 108%) for up to 422 days. Residues of CPU were also found to be stable in frozen mustard greens (average corrected stored recovery of 86%) for up to 520 days. However, residues of PCA were unstable (average corrected stored recovery of 17%) after 423 days of storage.

The results suggest that residues of PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of PCA residues for degradation during storage would not have a significant effect on the results of the submitted field trials because individual residues of diflubenzuron in/on mustard greens were on the average ~ 40x greater than those of PCA. These data are adequate to support the storage conditions and intervals of the field trial samples.

In mustard greens harvested 6-8 days following the last of three or four broadcast foliar applications of diflubenzuron, the combined residues of diflubenzuron, CPU, and PCA were <0.065 ppm-7.07 ppm. (Table C.3). The HAFT was 6.85 ppm and average residues were 2.05 ppm (Table C.4).

Common cultural practices were used to maintain the test crop. The weather conditions as well as maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron from Mustard Greens.**

| Analyte | Matrix | Spike level (ppm) | Sample size (n) | Recoveries (%) | Mean ± std dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Mustard Greens | 0.20 | 6 | 66, 78, 79, 85, 94, 97 | 83 ± 11 |
| | | 0.50 | 2 | 81, 83 | 82 |
| CPU [1] | | 0.02 | 8 | 75, 80, 80, 85, 85, 90, 95, 100 | 86 ± 8 |
| PCA | | 0.005 | 8 | 78, 78, 84, 84, 86, 88, 102, 105 | 88 ± 10 |
| **Method validation** | | | | | |
| Diflubenzuron | Mustard Greens | 0.05 | 3 | 67, 80, 88 | 78 ± 11 |
| | | 0.50 | 3 | 88, 90, 91 | 90 ± 2 |

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron from Mustard Greens.**

| Analyte | Matrix | Spike level (ppm) | Sample size (n) | Recoveries (%) | Mean ± std dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| CPU [1] | | 5.00 | 3 | 79, 81, 86 | 82 ± 4 |
| | | 0.01 | 3 | 80, 90, 90 | 87 ± 6 |
| | | 0.10 | 3 | 88, 88, 93 | 90 ± 3 |
| PCA | | 0.005 | 3 | 108, 112, 118 | 113 ± 5 |
| | | 0.05 | 2 | 112, 120 | 116 |

[1] CPU recoveries presented in the summary table of the submission do not match the recoveries presented in the raw data. It appears that the concurrent recoveries have been transposed with the method validation recoveries. The study reviewer has reported the recoveries from the raw data.

**TABLE C.2.1 Summary of Storage Conditions.**

| Analyte | Storage Temperature (°C) | Actual Storage Duration[1] (days) | Interval of Demonstrated Storage Stability (days) |
|---|---|---|---|
| Diflubenzuron | <0 | 422 | 422 |
| CPU | | 520 | 520 |
| PCA | | 423 | 423 |

[1] From harvest to extraction for analysis. Extracts were stored for up to 10 days before analysis.

**TABLE C.2.2 Stability of Diflubenzuron and its Metabolites in Frozen Mustard Greens.**

| Matrix | Analyte | Spike Level (ppm) | Storage interval (days) | Freshly Fortified Recovery (%) | Stored Sample Residues (%) | Average Corrected Stored Recovery (%) |
|---|---|---|---|---|---|---|
| Mustard Greens | Diflubenzuron | 0.5 | 422 | 75, 72, 83, 81 [78] | 83, 85 [84] | 108 |
| | CPU | 0.1 | 520 | 120, 114, 85, 95 [104] | 92, 85 [89] | 86 |
| | PCA | 0.05 | 423 | 108, 105, 105, 102 [105] | 18, 18 [18] | 17 |

**TABLE C.3. Residue Data from Mustard Green Field Trials with Diflubenzuron.**

| Trial ID (City, State; Year) | Zone | Crop Variety | Total Rate (lb ai/A) | PHI (Days) | Residues (ppm)[1] | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Diflubenzuron | CPU | PCA | Combined |
| Weslaco, TX 2001; TX27 | 6 | Florida Broadleaf | 0.256 | 6 | 1.02, 1.16 | <0.01, <0.01 | <0.005, <0.005 | 1.04, 1.18 |
| Tifton, GA 2001; GA20 | 2 | Curly Leaf | 0.190 | 7 | 0.82, 2.19 | <0.01, <0.01 | <0.005, <0.005 | 0.84, 2.21 |
| Tifton, GA 2001; GA21 | 2 | Florida Broadleaf | 0.254 | 8 | 1.95, 3.07 | <0.01, <0.01 | <0.005, <0.005 | 1.97, 3.09 |
| Salinas, CA 2001; CA76 | 10 | Southern Giant Curled | 0.258 | 6 | 1.08, 0.91 | <0.01, <0.01 | <0.005, <0.005 | 1.10, 0.93 |
| Salinas, CA 2001; CA77 | 10 | Southern Giant Curled | 0.253 | 7 | <0.05, <0.05 | <0.01, <0.01 | <0.005, <0.005 | <0.065, <0.065 |
| Celeryville, OH 2001; OH19 | 5 | Greenwave | 0.255 | 7 | 1.17, 1.24 | <0.01, <0.01 | <0.005, <0.005 | 1.19, 1.26 |
| Crossville, TN 2001; TN11 | 2 | Southern Giant Curled | 0.249 | 7 | 1.26, 2.89 | <0.01, <0.01 | <0.005, <0.005 | 1.28, 2.91 |
| Gainesville, FL 2001; FL37 | 3 | Southern Giant | 0.254 | 7 | 7.05, 6.60 | 0.018, 0.019 | <0.005, <0.005 | 7.07, 6.62 |

[1] The LOQ is 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA.

| TABLE C.4. Summary of Residue Data from Mustard Green Field Trials with Diflubenzuron. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Commodity | Total Applic. Rate (lb ai/A) | PHI (days) | Combined Residue Levels of Diflubenzuron, CPU, and PCA (ppm)[1] | | | | | | |
| | | | n | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Mustard Greens | 0.19-0.26 | 6-8 | 16 | <0.065 | 7.07 | 6.85 | 1.23 | 2.05 | 2.05 |

[1] The LOQ is 0.05 ppm for diflubenzuron, 0.01 ppm for CPU, and 0.005 ppm for PCA.
[2] HAFT = Highest-Average Field Trial.

## D. CONCLUSION

The residue data from the mustard green trials are adequate and support the use of the 2.0 lb/gal EC formulation of diflubenzuron on mustard greens for up to 4 foliar treatments at a total seasonal rate of 0.19-0.26 lb ai/A, a PHI of 6-8 days, and a retreatment interval of 8-15 days. The results show that the combined residues of diflubenzuron, CPU, and PCA were <0.065 ppm-7.07 ppm in/on mustard greens harvested 6-8 days following the last of 3 to 4 foliar treatments of a 2 lb/gal FIC test formulation for a total application rate of 0.19-0.26 lb ai/A. The HAFT was 6.85 ppm and the average combined residues were 2.05 ppm. No residue decline data were submitted.

## E. REFERENCES

None

## F. DOCUMENT TRACKING

RDI: RAB1 Chemists (8/23/06)
Petition Number(s): PP#5E6966
DP#: 321623
PC Code: 108201

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This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Durham, NC 27713; submitted 06/23/2006). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## STUDY REPORT:

46609501. Corley, J. (2005) Diflubenzuron: Magnitude of the Residue on Small Grain. Lab Project Number: 08024.02-PTR01. Unpublished study prepared by Interregional Research Project No. 4 (IR-4). 800 p.

## EXECUTIVE SUMMARY:

In a field trial conducted during the 2002 growing season in WA, diflubenzuron (2 lb/gal flowable concentrate (FlC)) was applied to a wheat crop (pre-booting growth stage) as one broadcast foliar application at rates of 0.066 or 0.646 lb ai/A. Single bulk samples of control and treated wheat grain were harvested at commercial maturity, 83 days after treatment (DAT). Wheat grain was processed into aspirated grain, germ, bran, flour, shorts and middlings using simulated commercial procedures. Prior to analysis, wheat grain and processed products were stored frozen for up to 90-113 days, and one wheat germ sample was stored for up 321 days prior to analysis of diflubenzuron. The storage conditions and intervals of processed samples are partially supported by adequate storage stability data. The available storage stability data for rice bran may be translated to wheat bran; however, additional storage stability data for wheat flour, middlings, shorts, and germ are required.

Samples of wheat grain and its processed commodities were analyzed for residues of diflubenzuron, 4-chlorophenylurea (CPU), and 4-chloroaniline (PCA), using high-performance liquid chromatography (HPLC)/ultraviolet (UV), gas chromatography/mass spectroscopy (GC/MS), and GC/MS with selected-ion monitoring (SIM), respectively. These methods, which are similar or based on method submissions previously deemed acceptable by the Agency, were adequately validated in conjunction with the field sample analyses. The lowest limit of method validations (LLMVs) are 0.05 ppm for diflubenzuron and 0.005 ppm for CPU and PCA in all wheat matrices.

The results show that following one application of the test formulation at 0.066 lb ai/A (1x), individual residues of diflubenzuron, CPU, and PCA were each below the respective LOQ in/on the raw agricultural commodity (RAC) (wheat grain) for a combined total of <0.06 ppm. The combined residues were <0.06 ppm in shorts, middlings, flour, bran, and germ, and were <2.104 ppm in aspirated grain fractions. These data indicate that the combined residues did not

concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 1x-treated wheat grain is >35.1x.

Following one application of the test formulation at 0.646 lb ai/A (10x), individual residues of diflubenzuron, CPU, and PCA were 0.147 ppm, <0.005 ppm, and <0.005 ppm, respectively in/on the RAC (wheat grain) for a combined total of <0.157 ppm. The combined residues were <0.085 ppm in shorts, <0.06 ppm in middlings, <0.06 ppm in flour, <0.104 ppm in bran, <0.061 ppm in germ, and <28.069 ppm in aspirated grain fractions. These data also indicate that the combined residues did not concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 10x-treated wheat grain is 180x.

**STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

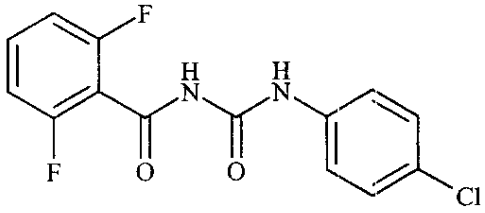
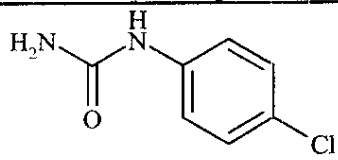
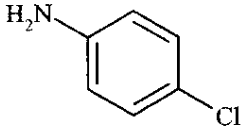
Under the conditions and parameters used in the study, the wheat processing data are classified as scientifically acceptable, pending submission of additional supporting storage stability data for wheat processed commodities. Storage stability data are required demonstrating the stability of diflubenzuron, CPU, and PCA residues in all wheat processed commodities, except bran, over the storage duration of the samples from the subject processing study. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 321623.

**COMPLIANCE:**

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. The study authors noted numerous minor deviations from GLP compliance at the trial site, including the collection of weather data and descriptions of the field plot. However, these deviations do not impact the validity of the study.

## A. BACKGROUND INFORMATION

Diflubenzuron is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The Reregistration Eligibility Decision (RED) for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008). Tolerances for residues of diflubenzuron are established under 40 CFR §180.377.

| **TABLE A.1. Diflubenzuron Nomenclature.** | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | Dimilin, Vigilante, Micromite, Adept |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Product (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461) |
| Regulated Metabolite |  |
| Common name | 4-chlorophenylurea (CPU) |
| Regulated Metabolite |  |
| Common name | 4-chloroaniline (PCA) |

| **TABLE A.2. Physicochemical Properties of Diflubenzuron.** | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | Not available | |
| Density | Not available | |
| Water solubility (25°C) | 0.08 ppm | |
| Solvent solubility (25°C) (ppm) | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25°C) | $1.2 \times 10^{-4}$ mPa | |
| Dissociation constant, $pK_a$ | Not available | |
| Octanol/water partition coefficient, $Log(K_{OW})$ | 3.89 | |
| UV/visible absorption spectrum | Not available | |

# B. EXPERIMENTAL DESIGN

## B.1. Application and Crop Information

**TABLE B.1.1. Trial Site Conditions.**

| Location: City, State; Year (Trial ID) | EP[1] | Application | | | | | Tank Mix/ Adjuvants |
|---|---|---|---|---|---|---|---|
| | | Method; Timing | Volume[2] | Single Rate (lb ai/A) | RTI[3] (days) | Total Rate (lb ai/A) | |
| Prosser, WA; 2002 (WA41) | 2 lb/gal FlC | One broadcast foliar application: Pre-boot stage | 13.66 | 0.066 | NA | 0.066 | None |
| | | One broadcast foliar application: Pre-boot stage | 13.66 | 0.646 | NA | 0.646 | |

[1] EP = End-use Product; DIMILIN® 2L
[2] Gallons per acre
[3] RTI = Retreatment Interval; not applicable (NA) because a single application was made at each treated plot.

## B.2. Sample Handling and Processing Procedures

Single bulk samples of control and treated wheat grain were harvested at normal crop maturity, 83 DAT. Samples were shipped frozen to the processing facility (Texas A&M University, Bryan, TX), where samples were processed into aspirated grain, germ, bran, flour, shorts and middlings using simulated commercial procedures. After processing, samples were collected, placed in frozen storage, and shipped frozen to the analytical laboratory (PTRL West, Inc., Hercules, CA) for analysis.

## B.3. Analytical Methodology

The wheat samples were analyzed for diflubenzuron, CPU, and PCA using a separate PTRL method for each analyte. The methods are described in "*Dimilin 25W, Dimilin 80WG, and Dimilin 2L in Almonds: Magnitude of Residue Study, J. Rose dated September 1999.*"

For analysis of diflubenzuron, samples are extracted twice with acetonitrile (ACN) and centrifuged. The supernatants are combined and partitioned with hexane. The ACN layer is concentrated to dryness, redissolved in ACN and water, and sequentially cleaned up on a C18 solid-phase extraction (SPE) column and silica-gel SPE column. After clean up, residues are analyzed by HPLC on a C8 or C18 column with UV detection. The diflubenzuron limits of detection (LODs) for wheat grain and bran were calculated to be 0.012 ppm and 0.023 ppm, respectively, and the calculated limits of quantitation (LOQs) were 0.037 ppm and 0.070 ppm, respectively. The LLMV for diflubenzuron was 0.05 ppm for each commodity.

For analysis of CPU, samples are dried with sodium sulfate and extracted with ethyl acetate. Residues are evaporated to dryness, redissolved in acetone and petroleum ether and cleaned up on a silica-gel SPE column. Again, residues are evaporated to dryness and redissolved in acetonitrile. The sample is filtered and derivatized in a glass tube with heptafluorobutyric anhydride for 10 minutes. Residues are then analyzed by GC/MS. For wheat grain, the LOD for CPU was calculated to be 0.002 ppm and the calculated LOQ was 0.006 ppm. The LLMV for CPU was 0.005 ppm for each commodity.

For analysis of PCA, residues are acidified with HCl and sonicated for 30 minutes at 60 °C. NaOH and NaCl are added, and residues are extracted three times with hexane. Residues are then partitioned with 0.1 N HCl, neutralized, and extracted with hexane. Extracts are dried and cleaned up with a Florisil column, derivatized with heptafluorobutyric acid for 10 minutes, after which water, sodium carbonate and hexane are added. Residues in the hexane layer are analyzed by GC/MS with SIM. The LOD for PCA in each wheat matrix was calculated to be 0.001 ppm and the calculated LOQ was either 0.003 or 0.004 ppm. The LLMV for PCA was 0.005 ppm for each commodity.

In conjunction with the analysis of processing samples, the above methods were validated using control samples of wheat matrices fortified with diflubenzuron, CPU or CPA at 0.005-0.5 ppm.

## C. RESULTS AND DISCUSSION

The analytical methods used to determine residues of diflubenzuron, CPU, and PCA in/on wheat grain and its processed commodities were adequately validated in conjunction with the sample analyses. Method recoveries from concurrent analysis of samples as well as from additional method verification (see Table C.1) were generally within the acceptable range of 70-120%. Three low recoveries (58-68%) were obtained for diflubenzuron in bran and germ, and for CPU in grain, but overall mean recoveries were acceptable. Apparent residues of diflubenzuron, CPU, and PCA were each <LOQ in/on the untreated samples of wheat grain, shorts, middlings, flour, bran, germ, and aspirated grain fractions. Adequate sample calculations and example chromatograms were provided.

Prior to analysis, wheat grain and processed products were stored frozen for up to 90-113 days, and one wheat germ sample was stored 321 days prior to analysis for diflubenzuron (Table C.2.1). A concurrent freezer storage stability study was conducted with the associated wheat field trials to validate sample storage conditions and intervals of the RAC (wheat grain). The results (Table C.2.2) show that residues of diflubenzuron are reasonably stable in/on frozen wheat grain (average corrected stored recovery of 105%) for up to 296 days. Residues of CPU were also found to be stable in frozen wheat grain (average corrected stored recovery of 85%) for up to 348 days. However, residues of PCA were unstable (average corrected stored recovery of 32%) after 293 days of storage. These data support the storage conditions of samples of wheat grain and aspirated grain fractions from the wheat processing study.

No supporting storage stability data were conducted for the wheat processed commodities. The available storage stability data (DP# 244487, G. Kramer, 2/17/1999) for processed rice bran indicate that diflubenzuron and CPU are stable over a ~12-month period, but that PCA is unstable in rice bran, degrading significantly after 1 month. These data may be translated to wheat bran.

The results suggest that residues of PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of PCA residues for degradation during storage would not have a significant effect on

the results of this processing study because individual residues of PCA in/on wheat grain and bran were all below <0.005 ppm.

The results of the wheat processing study show that following one application of the test formulation at 0.066 lb ai/A (1x), individual residues of diflubenzuron, CPU, and PCA were each below the respective LLMV in/on the RAC (wheat grain) for a combined total of <0.06 ppm. When the 1x-treated samples of wheat grain were processesed, the combined residues were <0.06 ppm in shorts, middlings, flour, bran, and germ and were <2.104 ppm in aspirated grain fractions. These data indicate that the combined residues did not concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 1x-treated wheat grain is >35.1x.

Following one application of the test formulation at 0.646 lb ai/A (1x), individual residues of diflubenzuron, CPU, and PCA were 0.147 ppm, <0.005 ppm, and <0.005 ppm, respectively in/on the RAC (wheat grain) for a combined total of <0.157 ppm. When the 10x-treated samples of wheat grain were processesed, the combined residues were <0.085 ppm in shorts, <0.06 ppm in middlings, <0.06 ppm in flour, <0.104 ppm in bran, <0.061 ppm in germ, and <28.069 ppm in aspirated grain fractions. These data also indicate that the combined residues did not concentrate in all processed fractions of wheat but did concentrate in aspirated grain fractions. The calculated processing factor for wheat aspirated grain fraction following processing of 10x-treated wheat grain is 180x.

**TABLE C.1. Summary of Method Recoveries of Diflubenzuron from Wheat.**

| Analyte | Matrix | Spike level (ppm) | Sample Size(n) | Recoveries (%) | Mean ± Std Dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Grain | 0.05-0.10 | 6 | 94, 95, 100, 106, 108, 116 | 103 ± 8 |
| CPU | | 0.005 | 6 | 80, 80, 80, 100, 100, 100 | 90 ± 11 |
| PCA | | 0.005 | 8 | 86, 94, 102, 104, 106, 106, 106, 110 | 102 ± 8 |
| Diflubenzuron | Bran | 0.05 | 2 | 68, 98 | 83 |
| CPU | | 0.01 | 2 | 90, 100 | 95 |
| PCA | | 0.005 | 2 | 96, 114 | 105 |
| Diflubenzuron | Flour | 0.50 | 2 | 99, 99 | 99 |
| CPU | | 0.01 | 2 | 70, 90 | 80 |
| PCA | | 0.005 | 2 | 96, 102 | 99 |
| Diflubenzuron | Germ | 0.05 | 2 | 86, 86 | 86 |
| CPU | | 0.01 | 2 | 70, 80 | 75 |
| PCA | | 0.005 | 2 | 96, 98 | 97 |
| Diflubenzuron | Middlings | 0.05 | 2 | 88, 100 | 94 |
| CPU | | 0.01 | 2 | 110, 120 | 115 |
| PCA | | 0.005 | 2 | 92, 96 | 94 |
| **Method validation** | | | | | |
| Diflubenzuron | Grain | 0.05-0.50 | 6 | 87, 94, 94, 96, 98, 101 | 95 ± 5 |
| CPU | | 0.005-0.05 | 6 | 58, 72, 80, 80, 100, 120 | 85 ± 22 |
| PCA | | 0.005-0.10 | 9 | 112, 112, 112, 114, 116, 117, 117, 119, 119 | 115 ± 3 |

**TABLE C.1. Summary of Method Recoveries of Diflubenzuron from Wheat.**

| Analyte | Matrix | Spike level (ppm) | Sample Size(n) | Recoveries (%) | Mean ± Std Dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Bran | 0.05-0.50 | 6 | 70, 74, 82, 84, 85, 91 | 81 ± 8 |
| CPU | | 0.005-0.05 | 6 | 82, 84, 94, 100, 100, 100 | 93 ± 8 |
| PCA | | 0.005-0.05 | 6 | 100, 102, 104, 105, 105, 107 | 104 ± 2 |
| Diflubenzuron | Flour | 0.05-0.50 | 6 | 84, 96, 98, 98, 98, 102 | 97 ± 7 |
| CPU | | 0.005-0.05 | 6 | 80, 100, 100, 102, 102, 108 | 99 ± 10 |
| PCA | | 0.005-0.05 | 6 | 100, 100, 100, 101, 104, 112 | 103 ± 5 |
| Diflubenzuron | Germ | 0.05-0.50 | 6 | 62, 70, 75, 83, 83, 84 | 76 ± 9 |
| CPU | | 0.005-0.05 | 6 | 80, 80, 80, 94, 100, 106 | 90 ± 12 |
| PCA | | 0.005-0.05 | 6 | 100, 102, 103, 104, 107, 110 | 104 ± 4 |

**TABLE C.2.1 Summary of Storage Conditions.**

| Analyte | Matrix | Storage Temperature (°C) | Actual Storage Duration (days) | Interval of Demonstrated Storage Stability (Days) |
|---|---|---|---|---|
| Diflubenzuron | Wheat, grain | <0 | 105 | 296 in/on wheat grain |
| | Aspirated Grain | | 98 | |
| | Shorts | | 113 | None available |
| | Middlings | | 113 | |
| | Flour | | 106 | |
| | Germ | | 321 | |
| | Bran | | 98 | 365 in/on rice bran |
| CPU | Wheat, grain | <0 | 100 | 348 in/on wheat grain |
| | Aspirated Grain | | 96 | |
| | Shorts | | 101 | None available |
| | Middlings | | 101 | |
| | Flour | | 111 | |
| | Germ | | 111 | |
| | Bran | | 96 | 338 in/on rice bran |
| PCA | Wheat, grain | <0 | 100 | 293 in/on wheat grain |
| | Aspirated Grain | | 92 | |
| | Shorts | | 90 | None available |
| | Middlings | | 90 | |
| | Flour | | 96 | |
| | Germ | | 96 | |
| | Bran | | 92 | 336 in/on rice bran with degradation (>45%) after 27 days |

[1] Storage from processing date to analysis date. Extracts were stored 1-4 days from extraction to analysis

**TABLE C.2.2 Stability of Diflubenzuron and its Metabolites in Frozen Wheat Matrices.**

| Matrix | Analyte | Spike Level (ppm) | Storage Interval (Days) | Freshly Fortified Recoveries (%) [Average] | Stored Sample Recoveries (%) [Average] | Average Corrected Stored Recoveries (%) |
|---|---|---|---|---|---|---|
| Grain | Diflubenzuron | 0.5 | 296 | 86, 86 [86] | 93, 88 [91] | 105 |
| | CPU | | 348 | 80, 80 [80] | 59, 77 [68] | 85 |
| | PCA | | 293 | 106, 102 [104] | 31, 35 [33] | 32 |

| TABLE C.3. Residue Data from Wheat Processing Study with Diflubenzuron. | | | | | |
|---|---|---|---|---|---|
| RAC | Processed Commodity | Total Rate (lb ai/A) | PHI (days) | Diflubenzuron + CPU + PCA = Combined Residues (ppm) | Processing Factor (Combined Residues) |
| Grain | RAC | 0.066 | 83 | <0.05 + <0.005 + <0.005 = <0.06 | -- |
| | Shorts | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Middlings | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Flour | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Bran | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Germ | | | <0.05 + <0.005 + <0.005 = <0.06 | 1x |
| | Aspirated grain | | | 2.094 + <0.005 + <0.005 = <2.104 | >35.1 |
| Grain | RAC | 0.646 | 83 | 0.147 + <0.005 + <0.005 = <0.157 | -- |
| | Shorts | | | 0.075 + <0.005 + <0.005 = <0.085 | 0.54x |
| | Middlings | | | <0.05 + <0.005 + <0.005 = <0.06 | 0.38x |
| | Flour | | | <0.05 + <0.005 + <0.005 = <0.06 | 0.38x |
| | Bran | | | 0.094 + <0.005 + <0.005 = <0.104 | 0.66x |
| | Germ | | | 0.051 + <0.005 + <0.005 = <0.061 | 0.42x |
| | Aspirated grain | | | 27.920 + 0.144 + <0.005 = <28.069 | 180x |

## D. CONCLUSION

The wheat processing study is acceptable pending submission of additional storage stability data for wheat processed commodities. The combined residues of diflubenzuron and its CPU and PCA metabolites do not appear to concentrate in shorts, middlings, flour, bran, and germ processed from wheat grain treated at 1x and 10x the field rate. The combined residues, however, concentrated >35.1x and 180x in aspirated grain fractions processed from wheat grain treated at 1x and 10x, respectively.

## E. REFERENCES

DP Barcodes: D253043, D253041, D244487, D251221 and D251609
Subject: PP#8F4925. Diflubenzuron (Dimilin® 2L, EPA Reg #400-461) on Rice. Amendments of 8/19/98, 11/20/98, 12/3/98, 1/21/99, 1/27/99 & 2/3/99. Analytical Method for Metabolites, Revised Label, Additional Residue, Storage Stability and Rotational Crop Data.
From: G. Kramer
To: M. Johnson/A. Sibold
Dated: 2/17/1999
MRIDs 44577601, 44689701-02, 44699201, 44692701, 44692703, 4469500102, and 44707401

## F. DOCUMENT TRACKING

RDI: RAB1 Chemists (8/23/06)
Petition Number(s): PP#5E6965
DP#: 321623
PC Code: 108201

Template Version June 2005

Primary Evaluator — Date: 14-SEP-2006
George F. Kramer, Ph.D., Senior Chemist
Registration Action Branch (RAB1)
Health Effects Division (HED) (7509C)

Approved by — Date: 14-SEP-2006
P.V. Shah, Ph.D. Branch Senior Scientist
RAB1/HED (7509C) for PV Shah

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Durham, NC 27713; submitted 06/23/2006). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## STUDY REPORT:

46609501. Corley, J. (2005) Diflubenzuron: Magnitude of the Residue on Small Grain. Lab Project Number: 08024.02-PTR01. Unpublished study prepared by Interregional Research Project No. 4 (IR-4). 800 p.

## EXECUTIVE SUMMARY:

Seven field trials on barley (2 winter and 5 spring varieties) and three trials on wheat (1 winter and 2 spring varieties) were conducted in EPA Zones 5, 7, 8 and 11 between the 2002 and 2003 growing seasons. At each location, diflubenzuron (2 lb/gal flowable concentrate (FlC)) was applied once to barley and wheat fields as a broadcast foliar application at 0.0592-0.0642 lb ai/A during crop development (pre-boot, pre-stem elongation, jointing, or Feekes 8 growth stage). A single control and duplicate treated samples of mature grain and straw were harvested from each site at 50-76 days after treatment (DAT). Hay was harvested from each site at 15-39 DAT, and wheat forage was harvested at 3-12 DAT. The collected samples of grain, straw, forage, and hay were stored frozen for up to 189, 232, 262 and 245 days, respectively, prior to residue analysis. The storage intervals and conditions are supported by adequate storage stability data.

The harvested commodities of barley and wheat were analyzed for residues of diflubenzuron, 4-chlorophenylurea (CPU), and 4-chloroaniline (PCA) using high-performance liquid chromatography (HPLC)/ultraviolet (UV), gas chromatography/mass spectroscopy (GC/MS), and GC/MS with selected-ion monitoring (SIM), respectively. These methods, which are similar or based on method submissions previously deemed acceptable by the Agency, were adequately validated in conjunction with the field sample analyses. The lowest limit of method validations (LLMVs) are 0.05 ppm for diflubenzuron and 0.005 ppm for CPU and PCA.

The results of the field trials indicate that following a single foliar application of the 2 lb/gal FlC formulation, the combined residues of diflubenzuron, CPU and PCA were: 0.13-1.47 ppm in/on barley hay (15-39 day PHI); <0.06 ppm in/on barley grain (50-76 day PHI); <0.06-0.58 ppm in/on barley straw (50-76 day PHI); 1.17-3.97 ppm in/on wheat forage (3-12 day PHI); 0.11-1.31 ppm in/on wheat hay (28-32 day PHI); <0.06 ppm in/on wheat grain (56-62 day PHI); and <0.06-1.04 ppm in/on wheat straw (56-62 day PHI). The combined highest-average field trial

(HAFT) values were: 1.40 ppm for barley hay; <0.06 ppm for barley grain; 0.57 ppm for barley straw, 3.80 ppm for wheat forage; 1.28 ppm for wheat hay; <0.06 ppm for wheat grain; and 0.91 ppm for wheat straw.

**STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the submitted residue data for barley and wheat commodities are scientifically acceptable. The acceptability of this study for regulatory purposes including the adequacy of the number and location of field trials will be addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP# 321623.

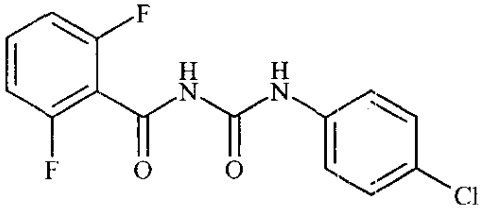
**COMPLIANCE:**

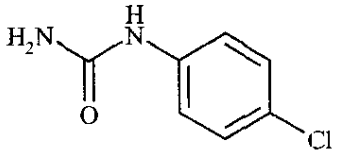
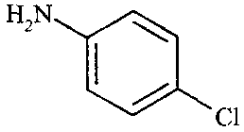
Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations were reported that would substantially impact the validity of the study.

## A. BACKGROUND INFORMATION

Diflubenzuron is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The Reregistration Eligibility Decision (RED) for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008). Tolerances for residues of diflubenzuron are established under 40 CFR §180.377.

**TABLE A.1. Diflubenzuron Nomenclature.**

| | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | Dimilin, Vigilante, Micromite, Adept |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Product (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461) |

| **TABLE A.1. Diflubenzuron Nomenclature.** | |
|---|---|
| Regulated Metabolite |  |
| Common name | 4-chlorophenylurea (CPU) |
| Regulated Metabolite |  |
| Common name | 4-chloroaniline (PCA) |

| **TABLE A.2. Physicochemical Properties of Diflubenzuron.** | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | Not available | |
| Density | Not available | |
| Water solubility (25 °C) | 0.08 ppm | |
| Solvent solubility (25 °C) (ppm) | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25 °C) | $1.2 \times 10^{-4}$ mPa | |
| Dissociation constant, $pK_a$ | Not available | |
| Octanol/water partition coefficient, $Log(K_{OW})$ | 3.89 | |
| UV/visible absorption spectrum | Not available | |

## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Barley and wheat were grown and maintained at each trial site (Table B.1.1) using typical agricultural practices for the respective geographical region. Information pertaining to soil conditions, temperature, and precipitation as well as irrigation for all sites was provided. Weather conditions were within normal variations for the region. Information was also provided on maintenance chemicals and other pesticides used at each site.

| **TABLE B.1.1. Trial Site Conditions.** | | | | |
|---|---|---|---|---|
| Trial Identification (City, State; Year) | Soil characteristics[1] | | | |
| | Type | %OM | pH | CEC (meq/g) |
| Fort Collins, CO; 2003 | Sandy Loam | 1.7 | 8.1 | 28.1 |
| Kimberly, ID; 2002 | Clay | 1.6 | 8.2 | NR |
| Aberdeen, ID; 2002 | Loamy Sand | 1.3 | 7.5 | NR |
| Kimberly, ID; 2002 | Silt Loam | 1.65 | 8.2 | NR |
| Minot, ND; 2003 | Loam | 3.4 | 4.7 | NR |
| Fargo, ND; 2003 | Silty Clay | 5.2 | 7.4 | NR |

**TABLE B.1.1. Trial Site Conditions.**

| Trial Identification (City, State; Year) | Soil characteristics[1] | | | |
|---|---|---|---|---|
| | Type | %OM | pH | CEC (meq/g) |
| Minot, ND; 2003 | Loam | 3.4 | 4.7 | NR |
| Fargo, ND; 2003 | Silty Clay | 5.2 | 7.4 | NR |
| Minot ND; 2003 | Loam | 3.8 | 6.0 | NR |
| Velva, ND; 2003 | Loam | 3.9 | 6.2 | 20.7 |
| Prosser, WA; 2002 | Loam | 1.1 | 6.3 | 12.8 |

[1] *OM = Organic matter, CEC = Cation-exchange capacity. These parameters are optional except in cases where their value affects the use pattern for the chemical.*
NR = Not Reported.

**TABLE B.1.2. Study Use Pattern on Barley and Wheat.**

| Location City, State; Year Trial ID | EP[1] | Application | | | | | Tank Mix/ Adjuvants |
|---|---|---|---|---|---|---|---|
| | | Method; Timing | Volume GPA | Single Rate (lb ai/A) | RTI[2] (days) | Total Rate (lb ai/A) | |
| Barley Field Trials | | | | | | | |
| Fort Collins, CO 2003; CO09 | 2 lb/gal FlC | One broadcast foliar application; Pre-boot | 12 | 0.0613 | NA | 0.0613 | None |
| Kimberly, ID 2002; ID12 | 2 lb/gal FlC | One broadcast foliar application; pre-stem elongation | 12 | 0.0592 | NA | 0.0592 | None |
| Aberdeen, ID 2002; ID13 | 2 lb/gal FlC | One broadcast foliar application; Pre-boot | 15 | 0.0620 | NA | 0.0620 | None |
| Minot, ND 2003; ND01 | 2 lb/gal FlC | One broadcast foliar application; jointing | 10 | 0.0629 | NA | 0.0629 | None |
| Fargo, ND 2003; ND02 | 2 lb/gal FlC | One broadcast foliar application; 5-6 leaves | 12 | 0.0621 | NA | 0.0621 | None |
| Minot, ND 2003; ND03 | 2 lb/gal FlC | One broadcast foliar application; jointing | 10 | 0.0619 | NA | 0.0619 | None |
| Velva, ND 2003; ND12 | 2 lb/gal FlC | One broadcast foliar application; Feekes 8 | 20 | 0.0628 | NA | 0.0628 | None |
| Wheat Field Trials | | | | | | | |
| Kimberly, ID 2002; ID14 | 2 lb/gal FlC | One broadcast foliar application; Pre-stem elongation | 13 | 0.0642 | NA | 0.0642 | None |
| | | | 13 | 0.621 | NA | 0.621 | None |
| Fargo, ND 2003; ND04 | 2 lb/gal FlC | One broadcast foliar application; 5-6 leaves | 12 | 0.0620 | NA | 0.0620 | None |
| Minot ND 2003; ND05 | 2 lb/gal FlC | One broadcast foliar application; jointing | 10 | 0.0619 | NA | 0.0619 | None |

[1] *EP = End-use Product; DIMILIN® 2L.*
[2] RTI = Retreatment Interval.

**TABLE B.1.3. Trial Numbers and Geographical Locations.**

| NAFTA Growing Zones [1] | Submitted | | Requested [2] | |
|---|---|---|---|---|
| | Barley | Wheat | Barley | Wheat |
| 1 | --- | --- | 1 [3] | --- |
| 2 | --- | --- | 1 [3] | 1 |
| 3 | --- | --- | --- | --- |
| 4 | --- | --- | --- | 1 |
| 5 | 1 | 1 | 3 | 5 |
| 6 | --- | --- | --- | 1 |
| 7 | 3 | 1 | 4 | 5 |
| 8 | 1 | --- | --- | 6 |
| 9 | --- | --- | 1 | --- |
| 10 | --- | --- | 1 | --- |
| 11 | 2 | 1 | 2 | 1 |
| 12 | --- | --- | --- | --- |
| Total | 7 | 3 | 12 | 20 |

[1] Zones 13-21 and 1A, 5A, 5B, and 7A were not included as the proposed use is for the US only.
[2] Suggested distribution of field trials when individual tolerances are sought for barley and wheat commodities (Source: Table 5 of OPPTS 860.1500.
[3] Either region/zone is acceptable.

## B.2. Sample Handling and Preparation

Single control and duplicate treated samples of barley hay, grain, and straw and wheat forage, hay, grain, and straw (amount not reported) were harvested from each trial site at appropriate stages for the commodity: barley hay 15-39 DAT, barley grain and straw 50-76 DAT, wheat forage 3-12 DAT, wheat hay 28-32 DAT, and wheat grain and straw 56-76 DAT. All samples were placed in frozen storage within 0.25-2.5 hours of collection. Field storage time was not documented. Samples were shipped frozen by ACDS freezer truck to the analytical laboratory (PTRL West, Hercules, CA) where samples were stored frozen at <0 °C until residue analysis.

## B.3. Analytical Methodology

The collected samples were analyzed for diflubenzuron, CPU, and PCA using a separate PTRL method for each analyte. The methods are described in "*Dimilin 25W, Dimilin 80WG, and Dimilin 2L in Almonds: Magnitude of Residue Study, J. Rose dated September 1999.*"

For analysis of diflubenzuron, samples are extracted twice with acetonitrile (ACN) (three times for wheat straw) and centrifuged. The supernatants are combined and partitioned with hexane. The ACN layer is concentrated to dryness, redissolved in ACN and water, and sequentially cleaned up on a C18 solid-phase extraction (SPE) column and silica-gel SPE column. After clean up, residues are analyzed by HPLC on a C8 or C18 column with UV detection. The limit of detection (LOD) for the diflubenzuron method for barley grain was calculated to be 0.027 ppm and the limit of quantitation (LOQ) was calculated to be 0.081 ppm. The diflubenzuron LODs for wheat grain and bran were calculated to be 0.012 ppm and 0.023 ppm, respectively, and the LOQs were 0.037 ppm and 0.070 ppm, respectively. The LLMV for diflubenzuron was 0.05 ppm for each commodity.

For analysis of CPU, samples are dried with sodium sulfate and extracted with ethyl acetate. Residues are evaporated to dryness, redissolved in acetone and petroleum ether and cleaned up on a silica-gel SPE column. Again, residues are evaporated to dryness and redissolved in acetonitrile. The sample is filtered and derivatized in a glass tube with heptafluorobutyric anhydride for 10 minutes. Residues are then analyzed by GC/MS. The LODs for the CPU method for barley grain and hay were calculated to be 0.001 ppm and 0.002 ppm, respectively, and the LOQs were calculated to be 0.004 ppm and 0.006 ppm, respectively. For wheat grain, the LOD for CPU was calculated to be 0.002 ppm and the LOQ was 0.006 ppm. The LLMV for CPU was 0.005 ppm for each commodity.

For analysis of PCA, residues are acidified with HCl and sonicated for 30 minutes at 60 °C. NaOH and NaCl are added, and residues are extracted three times with hexane. Residues are then partitioned with 0.1 N HCl, neutralized, and extracted with hexane. Extracts are dried and cleaned up with a Florisil column, derivatized with heptafluorobutyric acid for 10 minutes, after which water, sodium carbonate and hexane are added. Residues in the hexane layer are analyzed by GC/MS with SIM. The LODs for the PCA method for barley grain and straw were each calculated to be 0.001 ppm, and the LOQs were each calculated to be 0.003 ppm. The LOD for the PCA method in each wheat matrices was calculated to be 0.001 ppm and the LOQ was 0.001 ppm for wheat grain, 0.002 ppm for wheat hay, 0.003 ppm for barley hay, grain, and straw, wheat grain and straw, and wheat flour and germ, and 0.004 ppm for wheat bran. The LLMV for PCA was 0.005 ppm for each commodity.

In conjunction with the analysis of field trial samples, the above methods were validated using control samples of barley and wheat matrices fortified with diflubenzuron, CPU or PCA at 0.005-1.0 ppm.

## C. RESULTS AND DISCUSSION

Seven field trials on barley (2 winter and 5 spring varieties) and three trials on wheat (1 winter and 2 spring varieties) were conducted in EPA Zones 5, 7, 8 and 11 between the 2002 and 2003 growing seasons. At each location, a single application of diflubenzuron (2 lb/gal FlC) was made to barley and wheat fields as a broadcast foliar application at 0.0592-0.0642 lb ai/A during crop development (pre-boot, pre-stem elongation, jointing, or Feekes 8 growth stage). A single control and duplicate treated samples of mature grain and straw were harvested from each site at 50-76 DAT. Hay was harvested from each site at 15-39 DAT, and wheat forage was harvested at 3-12 DAT. The collected samples of grain, straw, forage, and hay were stored frozen for up to 189, 232, 262 and 245 days, respectively, prior to residue analysis. The storage intervals and conditions are supported by adequate storage stability data; a few recoveries were outside of this range but should not impact the validity of the method. Adequate examples calculation and samples chromatograms were provided.

Grain, straw, forage and hay samples were stored frozen for up to 189, 232, 262, and 245 days, respectively, prior to residue analysis (Table C.2.1). A freezer storage stability study was conducted to validate sample storage conditions and intervals. The results of this study (Table

C.2.2) indicate that diflubenzuron is reasonably stable in barley grain for 296 days, barley straw for 301 days, wheat forage for 422 days, and wheat hay for 337 days. CPU was reasonably stable in barley grain for 348 days and wheat forage for 267 days but showed a decline in barley straw (average corrected stored recovery of 34%) after 299 days and in wheat hay (average corrected stored recovery of 30%) after 355 days. PCA was reasonably stable in barley straw after 302 days, marginally stable in wheat hay after 359 days, and unstable in barley grain (average corrected stored recovery of 33%) and wheat forage (average corrected stored recovery of 39%) after 345 days.

The results suggest that residues of CPU and PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of CPU and PCA residues for degradation during storage would not have a significant effect on the results of the submitted field trials because individual residues of the metabolites in/on treated samples were mostly below the LLMV of 0.005 ppm.

The results of the field trials are presented in Tables C.3 and C.4. Following a single foliar application of the 2 lb/gal FlC formulation to the test crops, the combined residues of diflubenzuron and its CPU and PCA metabolites were: 0.13-1.47 ppm in/on barley hay (15-39 day PHI); <0.06 ppm in/on barley grain (50-76 day PHI); <0.06-0.58 ppm in/on barley straw (50-76 day PHI); 1.17-3.97 ppm in/on wheat forage (3-12 day PHI); 0.11-1.31 ppm in/on wheat hay (28-32 day PHI); <0.06 ppm in/on wheat grain (56-62 day PHI); and <0.06-1.04 ppm in/on wheat straw (56-62 day PHI). The combined HAFT values were: 1.40 ppm for barley hay; <0.06 ppm for barley grain; 0.57 ppm for barley straw, 3.80 ppm for wheat forage; 1.28 ppm for wheat hay; <0.06 ppm for wheat grain; and 0.91 ppm for wheat straw.

Common cultural practices were used to maintain the test crops. The weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data.

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron from Small Grains.**

| Analyte | Matrix | Spike Level (ppm) | Sample Size (n) | Recoveries (%) | Mean ± Std Dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Grain (barley and wheat) | 0.05-0.10 | 16 | 62, 86, 94, 95, 96, 100, 100, 106, 106, 108, 108, 108, 109, 114, 116, 116 | 102 ± 14 |
| CPU | | 0.005 | 14 | 60, 60, 60, 60, 60, 60, 80, 80, 80, 80, 80, 100, 100, 100 | 76 ± 16 |
| PCA | | 0.005 | 14 | 86, 94, 102, 104, 104, 106, 106, 106, 106, 108, 108, 110, 112, 120 | 105 ± 8 |
| Diflubenzuron | Hay (barley and wheat) | 0.1-1.0 | 12 | 66, 68, 71, 79, 80, 84, 87, 88, 107, 111, 120, 129 | 91 ± 21 |
| CPU | | 0.005-0.10 | 12 | 75, 84, 89, 100, 100, 100, 100, 101, 101, 109, 109, 119 | 99 ± 12 |
| PCA | | 0.005 | 10 | 98, 100, 102, 104, 106, 106, 112, 114, 114, 118 | 107 ± 7 |
| Diflubenzuron | Straw (barley | 0.05-0.20 | 12 | 62, 71, 76, 77, 81, 82, 84, 88, 90, 90, 93, 109 | 84 ± 12 |

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron from Small Grains.**

| Analyte | Matrix | Spike Level (ppm) | Sample Size (n) | Recoveries (%) | Mean ± Std Dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| CPU | and wheat) | 0.10 | 12 | 60, 60, 60, 80, 80, 90, 90, 90, 110, 120, 120, 120 | 90 ± 23 |
| PCA | | 0.005 | 12 | 96, 98, 102, 104, 104, 104, 108, 108, 110, 110, 112, 116 | 106 ± 6 |
| Diflubenzuron | Forage (wheat) | 0.05-1.0 | 4 | 84, 98, 102, 116 | 100 ± 13 |
| CPU | | 0.1 | 4 | 81, 84, 109, 112 | 97 ± 16 |
| PCA | | 0.005 | 4 | 98, 100, 106, 112 | 104 ± 6 |
| **Method Validation** | | | | | |
| Diflubenzuron | Grain (barley and wheat) | 0.05-0.5 | 6 | 87, 94, 94, 96, 98, 101 | 95 ± 5 |
| CPU | | 0.005-0.05 | 6 | 58, 72, 80, 80, 100, 120 | 85 ± 22 |
| PCA | | 0.005-0.10 | 9 | 112, 112, 112, 114, 116, 116, 117, 117, 119 | 115 ± 3 |
| Diflubenzuron | Hay (barley and wheat) | 0.05-0.5 | 6 | 82, 84, 86, 91, 94, 112 | 92 ± 11 |
| CPU | | 0.005-0.05 | 6 | 80, 80, 80, 92, 96, 98 | 88 ± 9 |
| PCA | | 0.005-0.05 | 6 | 104, 106, 106, 108, 108, 110 | 107 ± 2 |
| Diflubenzuron | Straw (barley and wheat) | 0.05-0.50 | 6 | 78, 78, 80, 81, 91, 104 | 85 ± 10 |
| CPU | | 0.005-0.05 | 6 | 80, 80, 80, 88, 88, 90 | 84 ± 5 |
| PCA | | 0.005-0.05 | 6 | 94, 97, 98, 103, 103, 111 | 101 ± 6 |

**TABLE C.2.1 Summary of Storage Conditions.**

| Matrix | Storage Temperature (°C) | Actual Storage Duration[1] (days) | Interval of Demonstrated Storage Stability (days) |
|---|---|---|---|
| Grain | <0 | 169-189 | 293-348 |
| Straw | | 166-232 | 299-302 |
| Forage | | 183-262 | 267-422 |
| Hay | | 205-245 | 251-359 |

[1] From harvest to extraction for analysis. Extracts were stored for up to 5 days before analysis

**TABLE C.2.2 Stability of Diflubenzuron and its Metabolites in Frozen Barley and Wheat Matrices.**

| Matrix | Analyte | Spike Level (ppm) | Storage Interval (Days) | Freshly Fortified Recoveries (%) [Average] | Stored Sample Recoveries (%) [Average] | Average Corrected Stored Recovery (%)[1] |
|---|---|---|---|---|---|---|
| Barley grain | Diflubenzuron | 0.5 | 0 | 108, 106 [107] | -- | -- |
| | | | 182 | 96, 99 [98] | 92, 79 [86] | 88 |
| | | | 296 | 86, 86 [86] | 93, 88 [91] | 105 |
| | CPU | | 0 | 80, 100 [90] | -- | -- |
| | | | 195 | 67, 71 [69] | 46, 60 [53] | 77 |
| | | | 348 | 80, 80 [80] | 59, 77 [68] | 85 |
| | PCA | | 0 | 108, 106 [107] | -- | -- |
| | | | 118 | 85, 89 [87] | 32, 50 [41] | 47 |
| | | | 293 | 106, 102 [104] | 31, 35 [33] | 33 |
| Barley straw | Diflubenzuron | 0.5 | 0 | 84, 76 [80] | -- | -- |
| | | | 134 | 72, 74 [73] | 73, 79 [76] | 104 |
| | | | 301 | 81, 61 [71] | 83, 84 [84] | 118 |
| | CPU | | 0 | 120, 120 [120] | -- | -- |
| | | | 233 | 77, 104 [91] | 40, 67 [54] | 59 |
| | | | 299 | 60, 90 [75] | 14, 37 [26] | 34 |
| | PCA | | 0 | 108, 110 [109] | -- | -- |
| | | | 168 | 104, 108 [106] | 88, 87 [88] | 88 |
| | | | 302 | 102, 108 [105] | 88, 91 [90] | 90 |
| Wheat forage | Diflubenzuron | 0.5 | 0 | 98, 84 [91] | -- | -- |
| | | | 245 | 84, 99 [92] | 72, 81 [77] | 83 |
| | | | 422 | 71, 64 [68] | 54, 67 [61] | 89 |
| | CPU | | 0 | 81, 84 [83] | -- | -- |
| | | | 267 | 105, 101 [103] | 90, 78 [84] | 84 |
| | PCA | | 0 | 98, 100 [99] | -- | -- |
| | | | 194 | 104, 109 [107] | 50, 56 [53] | 53 |
| | | | 345 | 100, 100 [100] | 38, 40 [39] | 39 |
| Wheat hay | Diflubenzuron | 0.5 | 0 | 107, 111 [109] | -- | -- |
| | | | 140 | 85, 86 [86] | 90, 85 [88] | 102 |
| | | | 337 | 80, 71 [76] | 80, 77 [79] | 103 |
| | CPU | | 0 | 100, 101 [101] | -- | -- |
| | | | 251 | 80, 85 [83] | 51, 57 [54] | 65 |
| | | | 355 | 80, 80 [80] | 21, 27 [24] | 30 |
| | PCA | | 0 | 102, 106 [104] | -- | -- |
| | | | 212 | 104, 107 [106] | 67, 70 [69] | 69 |
| | | | 359 | 110, 104 [107] | 75, 77 [76] | 76 |

[1] Average corrected recoveries were reported by the petitioner.

**TABLE C.3. Residue Data from Barley and Wheat Field Trials with Diflubenzuron.**

| Trial ID (City, State; Year) | Zone | Crop; Variety | Total Rate (lb ai/A) | PHI (days) | Matrix | Residues (ppm)[1] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | DFB | CPU | PCA | Combined |
| Kimberly, ID 2002 ID12 | 11 | Barley; Eight Twelve (Winter) | 0.0592 | 76 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 27 | Hay | 0.73, 0.75 | 0.006, 0.005 | <0.005, <0.005 | 0.74, 0.76 |
| | | | | 76 | Straw | 0.22, 0.14 | <0.005, <0.005 | <0.005, <0.005 | 0.23, 0.15 |
| Aberdeen, ID 2002 ID13 | 11 | Barley;Gallatin (Winter) | 0.0620 | 71 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 29 | Hay | 0.46, 0.81 | 0.011, 0.012 | <0.005, <0.005 | 0.47, 0.82 |
| | | | | 71 | Straw | 0.10, 0.13 | <0.005, <0.005 | <0.005, <0.005 | 0.11, 0.14 |
| Minot, ND 2003 ND01 | 7 | Barley; Robust (Spring) | 0.0629 | 55 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 28 | Hay | 0.25, 0.66 | 0.024, 0.034 | <0.005, <0.005 | 0.28, 0.70 |
| | | | | 55 | Straw | 0.30, 0.31 | <0.005, <0.005 | <0.005, <0.005 | 0.31, 0.32 |
| Fargo, ND 2003 ND02 | 5 | Barley;Robust (Spring) | 0.0621 | 54 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 31 | Hay | 0.52, 0.64 | 0.016, 0.015 | <0.005, <0.005 | 0.54, 0.66 |
| | | | | 54 | Straw | 0.44, 0.47 | <0.005, <0.005 | <0.005, <0.005 | 0.45, 0.48 |
| Minot, ND 2003 ND03 | 7 | Barley;Robust (Spring) | 0.0619 | 54 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 25 | Hay | 0.52, 0.70 | 0.038, 0.025 | <0.005, <0.005 | 0.56, 0.73 |
| | | | | 54 | Straw | 0.57, 0.55 | <0.005, <0.005 | <0.005, <0.005 | 0.58, 0.56 |
| Fort Collins, CO 2003 CO09 | 8 | Barley; Moravian 37 (Spring) | 0.0613 | 75 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 39 | Hay | 0.11, 0.11 | 0.018, 0.019 | <0.005, <0.005 | 0.13, 0.13 |
| | | | | 75 | Straw | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| Velva, ND 2003 ND12 | 7 | Barley; Foster (Spring) | 0.0628 | 50 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 15 | Hay | 1.31, 1.44 | 0.022, 0.031 | <0.005, <0.005 | 1.33, 1.47 |
| | | | | 50 | Straw | 0.54, 0.54 | 0.010, 0.013 | <0.005, <0.005 | 0.55, 0.56 |
| Kimberly, ID 2002 ID14 | 11 | Wheat; Brundage (Winter) | 0.0642 | 76 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 32 | Hay | 0.89, 0.86 | <0.005, <0.005 | <0.005, <0.005 | 0.90, 0.87 |
| | | | | 76 | Straw | 0.23, 0.34 | <0.005, <0.005 | <0.005, <0.005 | 0.24, 0.35 |
| | | | | 12 | Forage | 1.16, 2.48 | <0.005, <0.005 | <0.005, <0.005 | 1.17, 2.49 |
| | | | 0.621 | 76 | Grain | 0.064, 0.053 | <0.005, <0.005 | <0.005, <0.005 | 0.065, 0.074 |
| | | | | 32 | Hay | 18.4, 11.6 | 0.022, 0.015 | 0.005, <0.005 | 18.4, 11.6 |
| | | | | 76 | Straw | 6.52, 6.03 | 0.007, 0.011 | <0.005, <0.005 | 6.53, 6.04 |
| | | | | 12 | Forage | 11.7, 11.5 | 0.006, <0.005 | <0.005, <0.005 | 11.7, 11.5 |
| Fargo, ND 2003 ND04 | 5 | Wheat; Oxen (Spring) | 0.0620 | 56 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 31 | Hay | 1.24, 1.30 | 0.012, <0.005 | <0.005, <0.005 | 1.25, 1.31 |
| | | | | 56 | Straw | 0.77, 1.03 | 0.008, 0.008 | 0.006, 0.006 | 0.78, 1.04 |
| | | | | 5 | Forage | 2.64, 2.29 | <0.005, <0.005 | <0.005, <0.005 | 2.65, 2.30 |
| Minot ND 2003 ND05 | 7 | Wheat; Mountrail (Spring) | 0.0619 | 62 | Grain | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.06, <0.06 |
| | | | | 28 | Hay | 0.25, 0.10 | <0.005, <0.005 | <0.005, <0.005 | 0.26, 0.11 |
| | | | | 62 | Straw | <0.05, 0.07 | <0.005, <0.005 | <0.005, <0.005 | <0.06, 0.08 |
| | | | | 3 | Forage | 3.96, 3.61 | <0.005, <0.005 | <0.005, <0.005 | 3.97, 3.62 |

[1] The LLMV is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA.

| TABLE C.4. Summary of Residue Data from Barley and Wheat Field Trials with Diflubenzuron. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Commodity | Total Applic. Rate (lb ai/A) | PHI (days) | Combined Residues of Diflubenzuron, CPU, and PCA (ppm)[1] | | | | | | |
| | | | n | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Barley, hay | 0.0592-0.0629 | 15-39 | 14 | 0.13 | 1.47 | 1.40 | 0.68 | 0.67 | 0.38 |
| Barley, grain | | 50-76 | 14 | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | 0.0 |
| Barley, straw | | 50-76 | 14 | <0.06 | 0.58 | 0.57 | 0.32 | 0.33 | 0.20 |
| Wheat, forage | 0.0619-0.0642 | 3-12 | 6 | 1.17 | 3.97 | 3.80 | 2.57 | 2.70 | 1.00 |
| Wheat, hay | | 28-32 | 6 | 0.11 | 1.31 | 1.28 | 0.89 | 0.78 | 0.50 |
| Wheat, grain | | 56-62 | 6 | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | 0.0 |
| Wheat, straw | | 56-62 | 6 | <0.06 | 1.04 | 0.91 | 0.30 | 0.43 | 0.40 |

[1] The LLMV is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA.
[2] HAFT = Highest-Average Field Trial.

## D. CONCLUSION

The results of the field trials are adequate and will support use of the 2 lb/gal FlC formulation on barley and wheat for one foliar application at a maximum seasonal rate of 0.0592-0.0642 lb ai/A. The combined highest-average field trial (HAFT) values were: 1.40 ppm for barley hay; <0.06 ppm for barley grain; 0.57 ppm for barley straw, 3.80 ppm for wheat forage; 1.28 ppm for wheat hay; <0.06 ppm for wheat grain; and 0.91 ppm for wheat straw.

## E. REFERENCES

None.

## F. DOCUMENT TRACKING

RDI: RAB1 Chemists (8/23/06)
Petition Number(s): PP#5E6965
DP#: 321623
PC Code: 108201

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Date: 14-SEP-2006

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This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Durham, NC 27713; submitted 06/23/2006). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## STUDY REPORT:

46609401. Samoil, K. (2005) Diflubenzuron: Magnitude of the Residue on Peanut. Lab Project Number: 07737.01-PTR02. Unpublished study prepared by Interregional Research Project No. 4 (IR-4). 645 p.

## EXECUTIVE SUMMARY:

In a field trial conducted during the 2001 growing season in TX, diflubenzuron (2 lb/gal flowable concentrate (FlC)) was applied to peanuts as three broadcast foliar applications during the crop's developmental stage at ~0.125 lb ai/A/application for a total rate of 0.379 lb ai/A. Single bulk samples of untreated and treated peanuts were harvested at commercial maturity, 29 days after the last treatment (DAT). The harvested peanuts were dried, shelled, and processed into meal and refined oil using simulated commercial practices. Prior to analysis, peanut nutmeat, meal, and oil were stored frozen for 244-639 days; the storage intervals are supported by the concurrent storage stability data.

The peanut nutmeat and its processed commodities (meal and refined oil) were analyzed for residues of diflubenzuron using a high-performance liquid chromatography (HPLC)/ultraviolet (UV) method, for residues of 4-chlorophenylurea (CPU) using an HPLC/mass spectrometry (MS)/MS or UV method, and for residues of 4-chloroaniline (PCA) using a gas chromatography (GC)/MS method. These methods, which are similar or based on method submissions previously deemed acceptable by the Agency, were adequately validated in conjunction with the peanut sample analyses.

The results show that combined residues of diflubenzuron, CPU, and PCA were below the combined method LOQ (<0.06 ppm) in/on peanut nutmeat treated at a seasonal rate of 0.379 lb ai/A. Following processing of the treated nutmeat, the combined residues were below the method LOQs (<0.525 ppm) in peanut meal and <0.066 ppm (below the LOQ for diflubenzuron and PCA, and 0.011 ppm for CPU) in peanut oil. Processing factors for meal and oil could not be reliably calculated due to differing LOQs and <LOQ residues in all matrices (raw and unprocessed). Table 1 of OPPTS 860.1520 reports that the maximum theoretical concentration factor (by crop) is 3x for peanuts.

## STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the submitted peanut processing study is adequate to satisfy the guideline requirement for processed food/feed (Residue Chemistry Guideline OPPTS 860.1500). The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP# 321623.

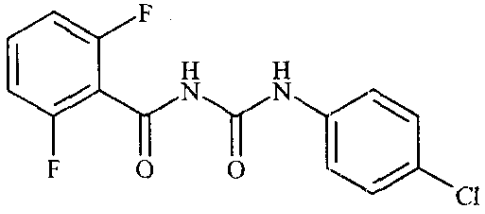
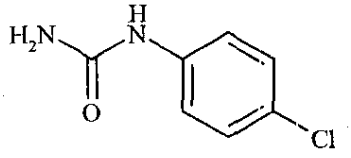
## COMPLIANCE:

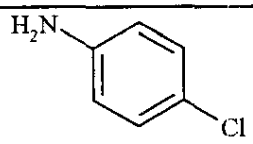
Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. The study authors noted numerous minor deviations from GLP compliance at the trial site, including the collection of weather data and descriptions of the field plot. However, these deviations do not impact the validity of the study.

## A. BACKGROUND INFORMATION

Diflubenzuron is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The Reregistration Eligibility Decision (RED) for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008). Tolerances for residues of diflubenzuron are established under 40 CFR §180.377.

**TABLE A.1. Diflubenzuron Nomenclature.**

| | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | *Dimilin, Vigilante, Micromite, Adept* |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Product (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461) |
| *Regulated Metabolite* |  |
| Common name | 4-chlorophenylurea (*CPU*) |

| TABLE A.1. Diflubenzuron Nomenclature. | |
|---|---|
| Regulated Metabolite |  |
| Common Name | 4-chloroaniline (PCA) |

| TABLE A.2. Physicochemical Properties of Diflubenzuron. | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | Not available | |
| Density | Not available | |
| Water solubility (25 °C) | 0.08 ppm | |
| Solvent solubility (25 °C) (ppm) | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25 °C) | $1.2 \times 10^{-4}$ mPa | |
| Dissociation constant, $pK_a$ | Not available | |
| Octanol/water partition coefficient, Log($K_{OW}$) | 3.89 | |
| UV/visible absorption spectrum | Not available | |

## B. EXPERIMENTAL DESIGN

### B.1. Application and Crop Information

| TABLE B.1.1. Trial Site Conditions. | | | | | | | |
|---|---|---|---|---|---|---|---|
| Location: City, State; Year (Trial ID) | EP [1] | Application | | | | | Tank Mix/ Adjuvants |
| | | Method; Timing | Volume (GPA) [2] | Single Rate (lb ai/A) | RTI [3] (days) | Total Rate (lb ai/A) | |
| Welasco, TX; 2001 (TX04) | 2 lb/gal FlC | Three broadcast foliar applications; first flower, flowering, nuts from first flowers pink | 14-17 | 0.121-0.132 | 13, 35 | 0.379 | None |

[1] EP = End-use Product; DIMILIN® 2L
[2] Gallons per acre
[3] RTI = Retreatment Interval

### B.2. Sample Handling and Processing Procedures

Single bulk samples of control and treated peanuts were harvested at normal crop maturity, 29 DAT, and dried in the field for 7-10 days. Collected samples were packed at ambient temperature and transported to the processing facility (Food Protein Research and Development Center, Bryan TX), where samples were processed using simulated commercial procedures. Samples were stored frozen (ca. -12 °C) until processing; processing was initiated 52 days after harvest of peanuts.

Peanuts were oven dried in the shell until the hull moisture was 7-12%; then shelled and the kernels oven dried to a moisture content of 7-10% and moisture-conditioned to 12%; the kernels were then heated to 93-104 °C and pressed to obtain crude oil. The remaining presscake (meal) was submerged in heated hexane three times, and then warm air was forced through to remove residual hexane. The crude oil mixture was heated to separate the crude oil and hexane, and the crude oil was refined separating the refined oil and soapstock. The refined oil was then bleached and deodorized. This process simulated industrial practice with the exception of a higher dry temperature and batch processing rather than continuous processing.

After processing, samples of meal and refined oil were collected, placed in frozen storage, and shipped along with the RAC subsample to PTRL West, Inc., Hercules CA for residue analysis. All samples were stored frozen (<0 °C) at PTRL until homogenization and analysis.

## B.3. Analytical Methodology

Peanut samples were analyzed for diflubenzuron, CPU, and PCA using separate methods based on those described in "*Dimilin 25W, Dimilin 80WD, and Dimilin 2L in Almonds: Magnitude of the Residue Study,*" Janine E. Rose, PTRL Study No, 723W, September 1999. Analysis for CPU in meal was done based on the method described in "Gas Chromatographic Determination of Diflubenzuron Metabolite A: Parachlorophenyl Urea in Mushrooms," D. Uhden, S.E. Kane, and M.A Morgenstern, Colorado Analytical Study No. 1248, November 20, 1995.

Samples of peanut nutmeat, meal, and oil were analyzed for diflubenzuron using an HPLC/UV method. Briefly, residues are extracted twice with ethyl acetate and then filtered. Residues are evaporated to dryness and redissolved in hexane. Residues are partitioned with acetonitrile (ACN) and again evaporated to dryness. Residues are redissolved with dichloromethane, and cleaned up on a Florisil solid-phase extraction (SPE) column. After clean up, residues are analyzed by HPLC on a C18 column with UV detection. The limit of quantitation (LOQ) is 0.05 ppm from nutmeat and oil, and 0.5 ppm for meal. The limit of detection (LOD) is 0.026 ppm for nutmeat, 0.072 ppm for meal and 0.016 ppm for oil.

Samples of peanut nutmeat and oil were analyzed for CPU using HPLC/MS/MS or HPLC/UV methods. Briefly, samples are extracted 3-5 times with ACN, and centrifuged or phase separated in a separatory funnel (oil). The supernatants (or ACN phases) are combined and partitioned with hexane. The ACN layer is concentrated to dryness, redissolved in ACN and water, and sequentially cleaned up on a C18 SPE column and silica gel SPE column. After clean up, residues in nutmeat and oil are analyzed by HPLC/MS/MS or HPLC/UV. The LOQ is 0.005 ppm for nutmeat and oil, and the LOD was not estimated.

Samples of peanut meal were analyzed for CPU using GC/MS method. Briefly, samples are dried with sodium sulfate and extracted with ethyl acetate. Residues are evaporated to dryness, redissolved in acetone and petroleum ether, and cleaned up on a silica gel SPE column. Again, residues are evaporated to dryness and redissolved in ACN. The sample is filtered and derivatized in a glass tube with heptafluorobutyric anhydride for 10 minutes. Residues are then analyzed by GC/MS. The LOQ is 0.02 ppm, and the LOD is 0.01 ppm for meal.

Samples of peanut nutmeat, meal, and oil were analyzed for PCA using a GC/MS method. Briefly, residues are acidified with HCl and sonicated for 30 minutes at 60 °C. NaOH and NaCl are added, and residues are extracted three times with hexane. Residues are then partitioned with 0.1 N HCl, neutralized and extracted with hexane. Extracts are dried and cleaned up with a Florisil column, derivatized with heptafluorobutyric acid for 10 minutes, after which water, sodium carbonate and hexane are added. Residues in the hexane layer are analyzed by GC/MS. The LOQ is 0.005 ppm for all matrices and the calculated LOD is 0.001 ppm.

In conjunction with the analysis of field trial and processing samples, the above methods were validated using control (or commercially obtained) samples of peanut matrices fortified with diflubenzuron, CPU or PCA at 0.005-1 ppm.

## C. RESULTS AND DISCUSSION

The HPLC/UV, HPLC/MS/MS or UV or GC/MS (for meal), and GC/MS methods used to determine residues of diflubenzuron, CPU, and PCA in/on peanut nutmeat, meal and oil were adequately validated in conjunction with the sample analyses. Method recoveries from concurrent analysis of samples as well as from additional method verification (see Table C.1) are within the acceptable range of 70-120% except for two samples of nutmeat which reported CPU recoveries of 64% and 68% and one sample of meal which reported CPU recoveries of 65%. In addition, method validation recoveries of diflubenzuron from meal at the 0.05 ppm fortification level reported only 32 ± 14% average recovery, therefore the method LOQ was increased to 0.5 ppm for diflubenzuron in meal. A single low method validation recovery (48%) was obtained for CPU in refined oil, but all other recoveries in oil were acceptable. Apparent residues of diflubenzuron, CPU, and PCA were each <LOQ in/on the untreated samples of nutmeat and meal, but residues of CPU in refined oil were 0.008 ppm in the control sample. Adequate sample calculations and example chromatograms were provided.

Prior to analysis, samples of peanut nutmeat, meal, and oil were stored frozen for 244-639 days (Table C.2.1). To validate sample storage conditions and intervals, a freezer storage stability study was conducted as part of the processing study. The results of this study (Table C.2.2) indicate that diflubenzuron (average corrected stored recoveries of 82-102%) is relatively stable in/on nutmeat for up to 295 days, in meal for up to 643 days, and in oil for up to 365 days. CPU and PCA also appear to be relatively stable (average corrected stored recoveries of 84-99%) in meal stored for up to 645 and 488 days, respectively, and in oil stored for up to 294 and 286 days, respectively. However, CPU (average corrected stored recovery of 67%) and PCA (average corrected stored recovery of 63%) exhibited 33-37% reduction in residues in nutmeat after 421 and 289 days of frozen storage, respectively.

The results suggest that residues of CPU and PCA should be corrected in nutmeat in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of CPU and PCA residues for degradation during storage would not have a significant effect on the results of the submitted study because individual residues of CPU and PCA in/on treated samples were mostly below the LOQ (<0.005 ppm). These data are adequate to support the storage conditions and intervals of samples from the processing study.

The results show that combined residues of diflubenzuron, CPU, and PCA were below the combined method LOQs (<0.06 ppm) in/on peanut nutmeat treated at a seasonal rate of 0.379 lb ai/A. Following processing of the treated nutmeat, the combined residues were below the method LOQs (<0.525 ppm) in peanut meal and <0.066 ppm (below the LOQ for diflubenzuron and PCA, and 0.011 ppm for CPU) in peanut oil. The petitioner stated that the residue value for CPU in peanut oil is suspect because apparent residues of CPU in untreated refined oil were 0.008 ppm. Processing factors for meal and oil could not be reliably calculated due to differing LOQs and <LOQ residues in all matrices (raw and unprocessed).

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron and its Metabolites *from Peanuts and Peanut Processed Commodities.***

| Analyte | Matrix | Spike level (ppm) | Sample size (n) | Recoveries (%) | Mean std dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Nutmeat | 0.05-0.2 | 13 | 74, 76, 76, 80, 80, 86, 86, 87, 90, 92, 94, 95, 102 | 86 ± 9 |
| | Meal | 0.5 | 2 | 84, 87 | 86 |
| | Refined oil | 0.05 | 2 | 87, 99 | 93 |
| CPU | Nutmeat | 0.01 | 14 | 64, 68, 70, 80, 80, 90, 90, 100, 100, 100, 110, 110, 120, 120 | 93 ± 19 |
| | Meal | 0.02 | 2 | 65, 85 | 75 |
| | Refined oil | 0.05 | 2 | 88, 120 | 104 |
| PCA | Nutmeat | 0.005 | 14 | 95, 97, 98, 98, 101, 102, 102, 105, 106, 106, 107, 108, 108, 110 | 103 ± 5 |
| | Meal | 0.005 | 2 | 95, 106 | 101 |
| | Refined oil | 0.005 | 2 | 93, 97 | 95 |
| **Method Validation** | | | | | |
| Diflubenzuron | Nutmeat | 0.05-1.0 | 9 | 81, 84, 85, 85, 97, 98, 102, 106, 116 | 95 ± 12 |
| | Meal | 0.05 | 3 | 15, 40, 40 | 32 ± 14 |
| | | 0.5-1.0 | 6 | 78, 79, 79, 82, 84, 85 | 81 ± 3 |
| | Refined oil | 0.05-1.0 | 9 | 77, 78, 79, 79, 80, 81, 81, 83, 84 | 80 ± 2 |
| CPU | Nutmeat | 0.005-0.1 | 9 | 80, 91, 92, 93, 96, 98, 100, 100, 100 | 94 ± 6 |
| | Meal | 0.02-0.1 | 9 | 72, 78, 86, 90, 92, 92, 95, 95, 95 | 88 ± 8 |
| | Refined oil | 0.005-0.1 | 9 | 48, 74, 78, 80, 84, 86, 93, 100, 100 | 83 ± 16 |
| PCA | Nutmeat | 0.005-0.1 | 9 | 100, 104, 110, 111, 112, 112, 113, 115, 120 | 111 ± 6 |
| | Meal | 0.005-0.1 | 9 | 90, 94, 94, 98, 102, 103, 104, 104, 105 | 99 ± 6 |
| | Refined oil | 0.005-0.1 | 9 | 96, 96, 98, 101, 102, 102, 104, 106, 111 | 102 ± 5 |

**TABLE C.2.1 Summary of Storage Conditions.**

| Analyte | Matrix | Storage Temperature (°C) | Actual Storage Duration[1] (days) | Interval of Demonstrated Storage Stability (days) |
|---|---|---|---|---|
| Diflubenzuron | Nutmeat | <0 | 244 | 295 |
| | Meal | | 629 | 643 |
| | Oil | | 276 | 365 |
| CPU | Nutmeat | | 408 | 421 |
| | Meal | | 639 | 345 |
| | Oil | | 270 | 294 |
| PCA | Nutmeat | | 266 | 289 |
| | Meal | | 254 | 488 |
| | Oil | | 252 | 286 |

[1] From harvest/processing to analysis; extracts were stored for up to 4 days before analysis. RAC samples were processed 52-56 days after harvest.

**TABLE C.2.2 Stability of Diflubenzuron and its Metabolites in Frozen Peanut Matrices.**

| Matrix | Analyte | Spike Level (ppm) | Storage interval (days) | Freshly Fortified Recovery (%) [Average] | Stored Sample Recovery (%) [Average] | Average Corrected Stored Recovery (%) |
|---|---|---|---|---|---|---|
| Nutmeat | Diflubenzuron | 0.5 | 295 | 75, 69 [72] | 65, 68 [67] | 93 |
| | CPU | 0.5 | 421 | 79, 84 [81] | 54, 53 [54] | 67 |
| | PCA | 0.1 | 289 | 70, 71 [71] | 41, 49 [45] | 63 |
| Meal | Diflubenzuron | 0.5 | 643 | 96, 86 [91] | 84, 65 [75] | 82 |
| | CPU | 0.5 | 645 | 110, 106 [108] | 90, 114 [102] | 94 |
| | PCA | 0.1 | 488 | 108, 106 [107] | 91, 88 [90] | 84 |
| Oil | Diflubenzuron | 0.5 | 365 | 115, 113 [114] | 114, 117 [116] | 102 |
| | CPU | 0.5 | 294 | 90, 81 [86] | 82, 87 [85] | 99 |
| | PCA | 0.1 | 286 | 68, 71 [70] | 65, 65 [65] | 93 |

**TABLE C.3. Residue Data from Peanut Processing Study with Diflubenzuron.**

| RAC | Processed Commodity | Total Rate (lb ai/A) | PHI (days) | Diflubenzuron + CPU + PCA = Combined Residues (ppm) | Processing Factor (Combined Residues) |
|---|---|---|---|---|---|
| Peanut | Nutmeat (RAC) | 0.379 | 29 | <0.05 + <0.005 + <0.005 = <0.06 | -- |
| | Meal | | | <0.5 + <0.02 + <0.005 = <0.525 | NC[1] |
| | Refined oil | | | <0.05 + 0.011 + <0.005 = <0.066 | NC |

[1] Processing factors could not reliably be calculated (NC) because most residues were below the respective LOQ for that matrix.

## D. CONCLUSION

The submitted peanut processing study is adequate. The results show that combined residues of diflubenzuron, CPU, and PCA were below the combined method LOQs (<0.06 ppm) in/on peanut nutmeat treated at a seasonal rate of 0.379 lb ai/A. Following processing of the treated nutmeat, the combined residues were below the method LOQs (<0.525 ppm) in peanut meal and <0.066 ppm (below the LOQ for diflubenzuron and PCA, and 0.011 ppm for CPU) in peanut oil. The petitioner stated that the residue value for CPU in peanut oil is suspect because apparent residues of CPU in untreated refined oil were 0.008 ppm. Processing factors for meal and oil could not be reliably calculated based on the results of this study.

## E. REFERENCES

None.

## F. DOCUMENT TRACKING

RDI: RAB1 Chemists (8/23/06)
Petition Number(s): PP#5E6967
DP#: 321623
PC Code: 108201

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Primary Evaluator — Date: 14-SEP-2006
George F. Kramer, Ph.D., Senior Chemist
Registration Action Branch (RAB1)
Health Effects Division (HED) (7509C)

Approved by — Date: 14-SEP-2006
P.V. Shah, Ph.D. Branch Senior Scientist
RAB1/HED (7509C) for PV Shah

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Durham, NC 27713; submitted 06/23/2006). The DER has been reviewed by HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

## STUDY REPORT:

46609401. Samoil, K. (2005) Diflubenzuron: Magnitude of the Residue on Peanut. Lab Project Number: 07737.01-TXP02. Unpublished study prepared by Interregional Research Project No. 4 (IR-4). 645 p.

## EXECUTIVE SUMMARY:

Twelve peanut field trials were conducted in EPA Zones 2, 3, and 6 during the 2001 growing season. At each trial location, diflubenzuron (2 lb/gal flowable concentrate (FlC)) was applied three times as broadcast foliar applications using ground equipment at 0.121-0.132 lb ai/A/application for a total rate of 0.373-0.385 lb ai/A. The first application was at first bloom, the second was 14 (± 1) days after the first, and the third was 28 (± 1) days before harvest at nine sites, 20 days at two sites and 26 days at one site. A single control and single.or duplicate treated samples of peanuts and peanut hay were harvested from each site at 20-28 days after treatment (DAT). Additional samples of peanut nutmeat and hay were collected from one site at 15, 20, 29, and 35 DAT to generate residue decline data. All samples were stored frozen for up to 481 days prior to residue extraction and analysis, an interval partially supported by available storage stability data.

The harvested samples were analyzed for residues of diflubenzuron using a high-performance liquid chromatography (HPLC)/ultraviolet (UV) method for nutmeat and hay, for residues of 4-chlorophenylurea (CPU) using HPLC/mass spectrometry (MS)/MS or UV for nutmeat or gas chromatography (GC)/MS methods for hay, and for residues of 4-chloroaniline (PCA) using GC/MS method for nutmeat and hay. These methods, which are similar or based on method submissions previously deemed acceptable by the Agency, were adequately validated in conjunction with the field sample analyses.

The results from three field sites (Trial IDs TN03, GA01, and GA03) showed possible sample contamination since residues of diflubenzuron or CPU in/on control samples of peanut nutmeat were equal to or higher than treated samples. No adequate explanation was provided except a statement from the petitioner commenting that the magnitude of residues in/on control samples which bore quantifiable residues was low relative to the residues in/on treated samples.

When samples from Trial IDs TN03, GA01, and GA03 are excluded, the combined residues of diflubenzuron, CPU and PCA ranged <0.060-<0.070 ppm in/on 18 samples of peanut nutmeat and 1.12-18.46 ppm in/on 11 samples of peanut hay that were harvested 20-28 days following the last of three foliar treatments of a 2 lb/gal FlC test formulation for a total application rate of 0.373-0.385 lb ai/A. The HAFT values were <0.070 ppm for nutmeat and 18.46 ppm for hay. The average combined residues were 0.06 ppm for nutmeat and 7.14 ppm for hay.

The submitted residue decline data for peanut nutmeat is inconclusive, and a trend could not be established because residues of the parent and its metabolites were all below the respective LOQs from samples collected at PHIs of 15, 20, 29, and 35 days. Although detectable residues in peanut hay were observed from the decline trial, a meaningful trend in residue decline could not also be established since residue levels fluctuated at various sampling intervals.

**STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS**:

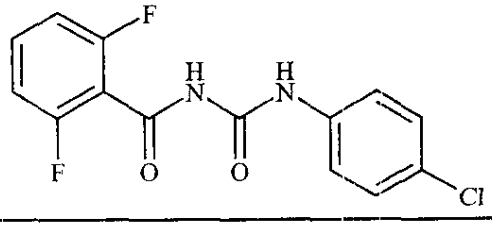
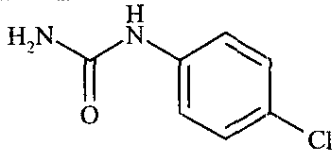
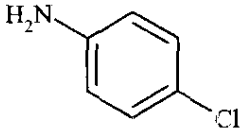
Under the conditions and parameters used in the study, the peanut field trial residue data are classified as partially acceptable to satisfy the guideline requirement for crop field trials (Residue Chemistry Guideline OPPTS 860.1500). The data from three GA trials are unacceptable because the reported diflubenzuron or CPU residues in/on control samples which were higher than those of treated samples. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP# 321623.

**COMPLIANCE:**

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations were reported that would substantially impact the validity of the study.

## A. BACKGROUND INFORMATION

Diflubenzuron is an insecticide/acaricide (insect growth regulator) that behaves as a chitin inhibitor to suppress the growth of many leaf-eating larvae, mosquito larvae, aquatic midges, rust mite, boll weevil, and flies. Diflubenzuron was first registered in the United States in 1979 for use as an insecticide. The Agency issued a Registration Standard for diflubenzuron in September, 1985, (NTIS #PB86-176500). Diflubenzuron was also the subject of a Residue Chemistry Chapter dated 11/16/84, an Addendum to the Registration Standard dated 12/4/84, and a Reregistration Standard Update dated 6/21/91. The Reregistration Eligibility Decision (RED) for diflubenzuron was issued in August, 1997 (EPA 738-R-97-008). Tolerances for residues of diflubenzuron are established under 40 CFR §180.377.

| **TABLE A.1. Diflubenzuron Nomenclature.** | |
|---|---|
| Compound |  |
| Common Name | Diflubenzuron |
| Trade and other Names | Dimilin, Vigilante, Micromite, Adept |
| IUPAC Name | 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea |
| CAS Name | *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide |
| CAS Registry Number | 35367-38-5 |
| End-Use Product (EP) | 2 lb/gal FlC formulation; DIMILIN® 2L (EPA Reg. No. 400-461) |
| Regulated Metabolite |  |
| Common name | 4-chlorophenylurea (CPU) |
| Regulated Metabolite |  |
| Common Name | 4-chloroaniline (PCA) |

| **TABLE A.2. *Physicochemical Properties of Diflubenzuron.*** | | |
|---|---|---|
| Parameter | Value | Reference |
| Melting range | 230-232 °C | http://www.arsusda.gov/acsl/services/ppdb/textfiles/DIFLUBENZURON |
| pH | *Not available* | |
| Density | Not available | |
| Water solubility (25 °C) | 0.08 ppm | |
| *Solvent solubility (25 °C) (ppm)* | $6.5 \times 10^3$ Acetone<br>$2 \times 10^3$ Acetonitrile<br>$2.4 \times 10^4$ Dioxane<br>$1.04 \times 10^5$ Dimethylformamide<br>$1.2 \times 10^5$ Dimethylsulfoxide<br>$1 \times 10^3$ Methanol<br>$6 \times 10^2$ Dichloromethane | |
| Vapor pressure (25 °C) | $1.2 \times 10^{-4}$ mPa | |
| Dissociation constant, $pK_a$ | Not available | |
| Octanol/water partition coefficient, $Log(K_{OW})$ | 3.89 | |
| UV/visible absorption spectrum | Not available | |

# B. EXPERIMENTAL DESIGN

## B.1. Study Site Information

Peanuts were grown and maintained at each trial site (Table B.1.1) using typical agricultural practices for the respective geographical region. Information pertaining to soil conditions, temperature, and precipitation was provided. Irrigation for all sites and weather conditions were within normal variations for the region. Information was also provided on the maintenance chemicals and other pesticides used at each site.

**TABLE B.1.1. Trial Site Conditions.**

| Trial Identification (City, State; Year) | Soil Characteristics[1] | | | |
|---|---|---|---|---|
| | Type | %OM | pH | CEC (meq/g) |
| Salisbury, MD; 2001 | Loamy Sand | 0.8 | 6.0 | NR |
| Crossville, TN; 2001 | Sandy Loam | 2.5 | 5.8 | NR |
| Crossville; TN2001 | Sandy Loam | 2.5 | 5.8 | NR |
| Rocky Mt, NC; 2001 | Sandy Loam | 1.2 | 6.0 | NR |
| Weslaco, TX; 2001 | Sandy Loam | 0.5 | 8.1 | NR |
| Weslaco, TX; 2001 | Sandy Loam | 0.5 | 8.1 | NR |
| Tifton, GA; 2001 | Sand | 0.67 | 6.2 | NR |
| Tifton, GA; 2001 | Sand | 0.67 | 6.2 | NR |
| Tifton, GA; 2001 | Sand | 0.67 | 6.2 | NR |
| Colony, OK; 2001 | Sand | 0.4 | 7.1 | NR |
| Salisbury, MD; 2001 | Sandy Loam | 1.1 | 6.2 | NR |
| Citra, FL; 2001 | Sand | 0.8 | 4.9-5.5 | NR |

[1] OM = Organic matter, CEC = Cation-exchange capacity. These parameters are optional except in cases where their value affects the use pattern for the chemical.
NR = Not Reported

**TABLE B.1.2. Study Use Pattern on Peanuts.**

| Location City, State; Year; Trial ID | EP[1] | Application | | | | | Tank Mix/ Adjuvants |
|---|---|---|---|---|---|---|---|
| | | Method; Timing | Volume GPA | Single Rate (lb ai/A) | RTI[2] (days) | Total Rate (lb ai/A) | |
| Salisbury, MD 2001; MD01 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, full bloom, some peanuts mature | 40-41 | 0.125-0.126 | 13, 14 | 0.376 | None |
| Crossville, TN 2001; TN03 | 2 lb/gal FlC | Three broadcast foliar applications; vegetative | 23-24 | 0.122-0.127 | 14, 28 | 0.374 | None |
| Crossville, TN2001; TN04 | 2 lb/gal FlC | Three broadcast foliar applications; vegetative | 23-24 | 0.125-0.126 | 14, 28 | 0.376 | None |
| Rocky Mt, NC 2001;NC01 | 2 lb/gal FlC | Three broadcast foliar applications; bloom, late bloom, pod-fill | 18-19 | 0.123-0.128 | 14, 32 | 0.377 | None |
| Weslaco, TX 2001; TX04 | 2 lb/gal FlC | Three broadcast foliar applications; first flower, flowering, nuts from first flowers pink | 14-17 | 0.121-0.132 | 13, 35 | 0.379 | None |
| Weslaco, TX 2001; TX05 | 2 lb/gal FlC | Three broadcast foliar applications; first flower, flowering, nuts from first flowers pink | 14-18 | 0.123-0.126 | 14, 30 | 0.374 | None |
| Tifton, GA 2001; GA01 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, bloom, immature peanuts | 20 | 0.125-0.127 | 15, 12 | 0.378 | None |

**TABLE B.1.2. Study Use Pattern on Peanuts.**

| Location City, State; Year; Trial ID | EP[1] | Application | | | | | Tank Mix/ Adjuvants |
|---|---|---|---|---|---|---|---|
| | | Method; Timing | Volume GPA | Single Rate (lb ai/A) | RTI[2] (days) | Total Rate (lb ai/A) | |
| Tifton, GA 2001; GA02 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, bloom, immature peanuts | 20 | 0.124-0.125 | 15, 18 | 0.374 | None |
| Tifton, GA 2001; GA03 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, bloom, immature peanuts | 20 | 0.124-0.126 | 15, 18 | 0.375 | None |
| Colony, OK 2001; OK01 | 2 lb/gal FlC | Three broadcast foliar applications; bloom, pegging, beginning maturity | 11 | 0.123-0.126 | 13, 34 | 0.373 | None |
| Salisbury, MD 2001; MD17 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, beginning to form pegs, beginning to form red skins | 41-68 | 0.124-0.127 | 14, 19 | 0.377 | None |
| Citra, FL 2001; FL52 | 2 lb/gal FlC | Three broadcast foliar applications; first bloom, vegetative bloom, fruiting | 15-16 | 0.126-0.132 | 13, 22 | 0.385 | None |

[1] EP = End-use Product; DIMILIN® 2L.
[2] RTI = Retreatment Interval.

**TABLE B.1.3. Trial Numbers and Geographical Locations.**

| NAFTA Growing Zones | Peanuts | | |
|---|---|---|---|
| | Submitted | Requested | |
| | | Canada | U.S. |
| 2 | 8 | --- | 8 |
| 3 | 1 | --- | 1 |
| 6 | 3[1] | --- | 2 |
| 8 | --- | --- | 1 |
| Total | 12 | NA | 12 |

[1] One trial was very near Zone 8 and will suffice to fulfill the geographic representation.

## B.2. Sample Handling and Preparation

Single control and treated samples of peanut hay and duplicate treated samples of peanuts (amount not reported) were harvested from each trial site at commercial maturity 20-28 days after the third application of the test formulation. Peanut plants were pulled or dug from the ground (by hand or using a mechanical digger). Hay was allowed to dry in the field before harvest to achieve a moisture content of 10-12%. Dried peanuts were shelled by hand or mechanical sheller. All samples were placed in frozen storage within 4.0 hours of collection. Field storage time was not documented. Samples were shipped frozen by ACDS freezer truck to the analytical laboratory (PTRL West, Hercules, CA) where samples were stored at <0 °C until extraction for analysis.

## B.3. Analytical Methodology

Samples were analyzed for diflubenzuron, CPU, and PCA using separate methods based on those described in "*Dimilin 25W, Dimilin 80WD, and Dimilin 2L in Almonds: Magnitude of the Residue Study,*" Janine E. Rose, PTRL Study No, 723W, September 1999. Due to analytical difficulties, CPU analysis for hay were done based on the method described in "Gas

Chromatographic Determination of Diflubenzuron Metabolite A: Parachlorophenyl Urea in Mushrooms," D. Uhden, S.E. Kane, and M.A Morgenstern, Colorado Analytical Study No. 1248, November 20, 1995.

Samples of peanut nutmeat and hay were analyzed for diflubenzuron using an HPLC/UV method. Briefly, residues are extracted twice with ethyl acetate and then filtered. Residues are evaporated to dryness and redissolved in hexane. Residues are partitioned with acetonitrile (ACN) and again evaporated to dryness. Residues are redissolved with dichloromethane, and cleaned up on a Florisil solid-phase extraction (SPE) column. After clean up, residues are analyzed by HPLC on a C18 column with UV detection. The limit of quantitation (LOQ) is 0.05 ppm from nutmeat and 0.1 ppm from hay, the calculated limit of detection (LOD) is 0.026 ppm for nutmeat and was not calculated for hay.

Samples of peanut nutmeat were analyzed for CPU using HPLC/MS/MS or HPLC/UV method. Briefly, samples are extracted twice with ACN and centrifuged. The supernatants are combined and partitioned with hexane. The ACN layer is concentrated to dryness, redissolved in ACN and water, and sequentially cleaned up on a C18 SPE column and silica-gel SPE column. After clean up, residues are analyzed by HPLC/MS/MS or HPLC/UV. The LOQ is 0.005 ppm for nutmeat, the LOD was not calculated.

Samples of peanut hay were analyzed for CPU using a GC/MS method. Briefly, samples are dried with sodium sulfate and extracted with ethyl acetate. Residues are evaporated to dryness, redissolved in acetone and petroleum ether, and cleaned up on a silica-gel SPE column. Again, residues are evaporated to dryness and redissolved in ACN. The sample is filtered and derivatized in a glass tube with heptafluorobutyric anhydride for 10 minutes. Residues are then analyzed by GC/MS. The LOQ is 0.01 ppm for hay, the LOD was not calculated.

Samples of peanut nutmeat and hay were analyzed for PCA using a GC/MS method. Briefly, residues are acidified with HCl and sonicated for 30 minutes at 60 °C. NaOH and NaCl are added, and residues are extracted three times with hexane. Residues are then partitioned with 0.1 N HCl, neutralized and extracted with hexane. Extracts are dried and cleaned up with a Florisil column, derivatized with heptafluorobutyric acid for 10 minutes, after which water, sodium carbonate and hexane are added. Residues in the hexane layer are analyzed by GC/MS. The LOQ is 0.005 ppm for nutmeat and hay and the calculated LOD is 0.001 ppm.

In conjunction with the analysis of field trial samples, the above methods were validated using control samples of peanut nutmeat and hay fortified with diflubenzuron, CPU or PCA at 0.005-20 ppm.

## C. RESULTS AND DISCUSSION

In 12 peanut field trials conducted during 2001, diflubenzuron (2 lb/gal FlC) was applied three times to fields as broadcast foliar applications using ground equipment at 0.121-0.132 lb ai/A/application during crop development. A single control and single or duplicate treated

samples of mature peanut and peanut hay were harvested from each site at 20-28 DAT. At one site, samples were also collected at 15, 20, 29, and 35 DAT to assess residue decline.

The HPLC/UV (for nutmeat and hay), HPLC/MS/MS or UV (for nutmeat) or GC/MS (for hay), and GC/MS (for nutmeat and hay) methods used to determine residues of diflubenzuron, CPU, and PCA in/on peanut nutmeat and hay were adequately validated in conjunction with the field sample analyses. Method recoveries from concurrent analysis of samples as well as from additional method verification (see Table C.1) are well within the acceptable range of 70-120% except for two samples of nutmeat which reported CPU recoveries of 64% and 68% and one sample of peanut hay which reported CPU recoveries of 50%. In addition, method validation recoveries of diflubenzuron from hay at the 0.05 ppm fortification level reported only 9 ± 1% average recovery; however, residue values of diflubenzuron in hay were well above this level from field samples. Adequate examples calculation and samples chromatograms were provided.

Samples of peanut nutmeat and hay samples were stored frozen for up to 481 days prior to residue extraction and analysis (Table C.2.1). To validate sample storage conditions and intervals, a freezer storage stability study was conducted as part of the residue field study. The results of this study (Table C.2.2) indicate that diflubenzuron (average corrected stored recovery of 93%) is relatively stable in/on nutmeat for up to 295 days; however, CPU (average corrected stored recovery of 67%) and PCA (average corrected stored recovery of 63%) exhibited 33-37% reduction in residues after 421 and 289 days of frozen storage, respectively. A similar storage stability profile was observed for peanut hay. Diflubenzuron (average corrected stored recovery of 82%) is relatively stable in/on hay for up to 356 days; CPU (average corrected stored recovery of 29%) and PCA (average corrected stored recovery of 75%) exhibited 25-71% reduction in residues after 484 and 338 days of frozen storage, respectively.

The results suggest that residues of CPU and PCA should be corrected in order to determine the residue levels that were present at the time of sample collection. However, HED has determined that correction of CPU and PCA residues for degradation during storage would not have a significant effect on the results of the submitted field trials because individual residues of CPU and PCA in/on treated samples were mostly below the LOQ (<0.005 ppm). These data are adequate to support the storage conditions and intervals of the field trial samples.

Following application of diflubenzuron totaling 0.373-0.385 lb ai/A, the combined residues of diflubenzuron, CPU and PCA were <0.060-<0.070 ppm in/on 18 samples of peanut nutmeat harvested 20-28 DAT. Combined residues were 1.12-18.46 ppm in/on 11 treated samples of peanut hay (Table C.3.). HAFT values were <0.070 ppm for nutmeat and 18.46 ppm for hay; average combined residues were 0.06 ppm for nutmeat and 7.14 ppm for hay (Table C.4). In three different trials, residues of diflubenzuron or CPU in peanut nutmeat were equal to or higher in control samples than treated samples; these residues were not included in the calculations from Table C.4.

The submitted residue decline data for peanut nutmeat is inconclusive, and a trend could not be established because residues of the parent and its metabolites were all below the respective LOQs at PHIs of 15, 20, 29, and 35 days. Although detectable residues in peanut hay were

observed from the decline trial, a meaningful trend with regard to residue decline could not also be established since residue levels fluctuated at various sampling intervals.

Common cultural practices were used to maintain the test crop. The weather conditions did not have a notable impact on the residue data. It is unclear whether or not the maintenance chemicals played a role in the high levels of CPU residues found in the TN03 and GA01 trials sites, as CPU is a metabolite of the maintenance chemical PCNB, and may have contributed to high residue levels in control samples. Other trial sites which also used this maintenance chemical did not experience high residues of CPU in control samples.

**TABLE C.1. Summary of Concurrent and Method Recoveries of Diflubenzuron from Peanuts.**

| Analyte | Matrix | Spike level (ppm) | Sample size (n) | Recoveries (%) | Mean std dev (%) |
|---|---|---|---|---|---|
| **Concurrent** | | | | | |
| Diflubenzuron | Nutmeat | 0.05 | 4 | 74, 76, 80, 86 | 79 ± 5 |
| | | 0.1 | 7 | 80, 86, 90, 94, 95, 97, 102 | 92 ± 7 |
| | | 0.2 | 2 | 76[1], 92[1] | 84 |
| CPU | | 0.01 | 14 | 64, 68, 70, 80, 80, 90, 90, 100, 100, 100, 110, 110, 120, 120 | 93 ± 19 |
| PCA | | 0.005 | 14 | 95, 97, 98, 98, 101, 102, 102, 105, 106, 106, 107, 108, 108, 110 | 103 ± 5 |
| Diflubenzuron | Hay | 0.1 | 4 | 70[1], 84[1], 88[1], 102[1] | 86 ± 13 |
| | | 0.5 | 5 | 72[1], 72, 76, 79, 81[1] | 76 ± 4 |
| CPU | | 0.02 | 6 | 76, 78, 80[1], 80[1], 102, 109 | 88 ± 14 |
| | | 0.10 | 1 | 99 | 99 |
| PCA | | 0.005 | 2 | 110, 118 | 114 |
| | | 0.020 | 6 | 90, 93, 94, 97, 98, 101 | 96 ± 4 |
| **Method validation** | | | | | |
| Diflubenzuron | Nutmeat | 0.05 | 3 | 102, 106, 116 | 108 ± 7 |
| | | 0.5 | 3 | 84, 85, 85 | 85 ± 1 |
| | | 1.0 | 3 | 81, 97, 98 | 92 ± 10 |
| CPU | | 0.005 | 3 | 80, 100, 100 | 93 ± 12 |
| | | 0.05 | 3 | 96, 98, 100 | 98 ± 2 |
| | | 0.1 | 3 | 91, 92, 93 | 92 ± 1 |
| PCA | | 0.005 | 3 | 100, 104, 120 | 108 ± 11 |
| | | 0.05 | 3 | 111, 112, 113 | 112 ± 1 |
| | | 0.10 | 3 | 110, 112, 115 | 112 ± 3 |
| Diflubenzuron | Hay | 0.05 | 3 | 8, 10, 10 | 9 ± 1 |
| | | 0.5 | 3 | 88, 89, 91 | 89 ± 2 |
| | | 1.0 | 3 | 98, 103, 104 | 102 ± 3 |
| | | 20[2] | 3 | 85, 87, 92 | 88 ± 4 |
| CPU | | 0.01 | 3 | 50[1], 100[1], 110[1] | 87 ± 32 |
| | | 0.1 | 3 | 93[1], 93[1], 100[1] | 95 ± 4 |
| PCA | | 0.005 | 3 | 106, 108, 110 | 108 ± 2 |
| | | 0.05 | 3 | 100, 112, 115, | 109 ± 8 |
| | | 0.10 | 3 | 96, 103, 118 | 106 ± 11 |

[1] Reported recoveries were corrected by the petitioner for apparent residue in control samples.
[2] Recoveries of samples fortified with diflubenzuron at 20 ppm were only reported in the summary table of the submission.

**TABLE C.2.1 Summary of Storage Conditions.**

| Analyte | Storage Temperature (°C) | Matrix | Actual Storage Duration[1] (days) | Interval of Demonstrated Storage Stability (days) |
|---|---|---|---|---|
| Diflubenzuron | <0 | Nutmeat | 244 | 295 |
| | | Hay | 349 | 356 |
| CPU | | Nutmeat | 408 | 421 |
| | | Hay | 481 | 484 |
| PCA | | Nutmeat | 266 | 289 |
| | | Hay | 323 | 338 |

[1] From harvest to extraction for analysis. Extracts were stored for up to 9 days before analysis

**TABLE C.2.2 Stability of Diflubenzuron and its Metabolites in Frozen Peanut Matrices.**

| Matrix | Analyte | Spike Level (ppm) | Storage interval (days) | Freshly Fortified Recovery (%) | Stored Sample Residues (%) | Average Corrected Stored Recovery (%) |
|---|---|---|---|---|---|---|
| Nutmeat | Diflubenzuron | 0.5 | 295 | 75, 69 [72] | 65, 68 [67] | 93 |
| | CPU | 0.5 | 421 | 79, 84 [81] | 54, 53 [54] | 67 |
| | PCA | 0.1 | 289 | 70, 71 [71] | 41, 39 [45] | 63 |
| Hay | Diflubenzuron | 0.5 | 356 | 95, 103 [99] | 83, 79 [81] | 82 |
| | CPU | 0.5 | 484 | 88, 108 [98] | 21, 35 [28] | 29 |
| | PCA | 0.1 | 338 | 102, 99 [101] | 77, 76 [76] | 75 |

**TABLE C.3. Residue Data from Peanut Field Trials with Diflubenzuron.**

| Trial ID (City, State; Year) | Zone | Crop Variety | Total Rate (lb ai/A) | Matrix | PHI (days) | Residues (ppm)[1] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Diflubenzuron | CPU | PCA | Combined |
| Salisbury, MD 2001 MD01 | 2 | VA-C98R | 0.376 | Nut | 28 | <0.05, <0.05 | <0.005, 0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | | No sample | No sample | No sample | No sample |
| Crossville, TN 2001 TN03 | 2 | VA 98R | 0.374 | Nut | 28 | <0.05, <0.05 | 0.011[2], 0.019[2] | <0.005, <0.005 | <0.066[2], <0.074[2] |
| | | | | Hay | | 18.39 | 0.052 | 0.016 | 18.46 |
| Crossville, TN 2001 TN04 | 2 | VA-C92R | 0.376 | Nut | 28 | 0.059, 0.060 | <0.005, <0.005 | <0.005, <0.005 | <0.069, <0.070 |
| | | | | Hay | | 10.69 | 0.065 | 0.037 | 10.79 |
| Rocky Mt, NC 2001 NC01 | 2 | VA 98R | 0.377 | Nut | 28 | <0.05, 0.055 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.065 |
| | | | | Hay | | 17.00 | 0.018 | 0.018 | 17.04 |
| Weslaco, TX 2001 TX04 | 6 | Florunner | 0.379 | Nut | 15 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | | 20 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | | 29 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | | 35 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | 15 | 11.03 | 0.029 | 0.017 | 11.08 |
| | | | | | 20 | 9.61 | 0.012 | 0.021 | 9.64 |
| | | | | | 29 | 8.39 | <0.01 | 0.015 | <8.42 |
| | | | | | 35 | 10.31 | 0.017 | 0.021 | 10.35 |
| Weslaco, TX 2001 TX05 | 6 | Florunner | 0.374 | Nut | 28 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | | 7.86 | 0.019 | 0.021 | 7.90 |
| Tifton, GA 2001 GA01 | 2 | NCV11 | 0.378 | Nut | 26 | <0.05, <0.05 | <0.005[2], <0.005[2] | <0.005, <0.005 | <0.060[2], <0.060[2] |
| | | | | Hay | | 2.64 | 0.012 | 0.047 | 2.70 |

**TABLE C.3. Residue Data from Peanut Field Trials with Diflubenzuron.**

| Trial ID (City, State; Year) | Zone | Crop Variety | Total Rate (lb ai/A) | Matrix | PHI (days) | Residues (ppm)[1] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Diflubenzuron | CPU | PCA | Combined |
| Tifton, GA 2001 GA02 | 2 | C99R | 0.374 | Nut | 20 | 0.052, 0.060 | <0.005, <0.005 | <0.005, <0.005 | <0.062, <0.070 |
| | | | | Hay | | 1.05 | 0.013 | 0.054 | 1.12 |
| Tifton, GA 2001 GA03 | 2 | Georgia Green | 0.375 | Nut | 20 | 0.072[2], 0.097[2] | <0.005, <0.005 | <0.005, <0.005 | <0.082[2], <0.107[2] |
| | | | | Hay | | 1.11 | 0.024 | 0.046 | 1.18 |
| Colony, OK 2001 OK01 | 6 | Tamspan | 0.373 | Nut | 27 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | | 1.64 | 0.019 | 0.013 | 1.67 |
| Salisbury, MD 2001 MD17 | 2 | VA-C98R | 0.377 | Nut | 28 | <0.05, <0.05 | <0.005, <0.005 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | | 7.11 | 0.046 | 0.017 | 7.17 |
| Citra, FL 2001 FL 52 | 3 | Florunner | 0.385 | Nut | 28 | <0.05, <0.05 | <0.005, 0.006 | <0.005, <0.005 | <0.060, <0.060 |
| | | | | Hay | | 1.89 | 0.025 | 0.137 | 2.05 |

[1] The LOQ is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA in nutmeat. The LOQ is 0.05 ppm for residues of diflubenzuron, 0.01 ppm for residues of CPU, and 0.005 ppm for residues of PCA in hay.
[2] Residues found in control samples were greater than that of treated samples; these values were excluded from calculations in Table C.4. Control samples from GA03 bore residues of diflubenzuron at 0.097 ppm and 0.084 ppm; control samples from TN03 bore residues of CPU at 0.022 ppm and 0.026 ppm; control samples from GA01 bore residues of CPU at 0.015 ppm and 0.006 ppm.

**TABLE C.4. Summary of Combined Residue Data from Peanut Field Trials with Diflubenzuron.**

| Commodity | Total Applic. Rate (lb ai/A) | PHI (days) | Residue Levels (ppm)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | n | Min. | Max. | HAFT[2] | Median | Mean | Std. Dev. |
| Nutmeat | 0.373-0.385 | 20-28 | 18 | <0.060 | <0.070 | <0.070 | 0.060 | 0.060 | 0.0 |
| Hay | | | 11 | 1.12 | 18.46 | 18.46 | 7.17 | 7.14 | 6.24 |

[1] The LOQ is 0.05 ppm for residues of diflubenzuron, and 0.005 ppm for residues of CPU and PCA in nutmeat.
[2] HAFT = Highest-Average Field Trial.

## D. CONCLUSION

The peanut field trial data are partially acceptable to support the use of diflubenzuron on peanuts for up to three foliar treatments at a total seasonal rate of 0.375 lb ai/A, a PHI of 20-28 days, and a retreatment interval of 12-35 days. The data from three field sites (Trial IDs TN03, GA01, and GA03) are unacceptable because the reported diflubenzuron or CPU residues in/on control samples which were higher than those of treated samples. The combined residues of diflubenzuron, CPU and PCA ranged <0.060-<0.070 ppm in/on 18 samples of peanut nutmeat and 1.12-18.46 ppm in/on 11 samples of peanut hay that were harvested 20-28 days following the last of three foliar treatments of a 2 lb/gal FlC test formulation for a total application rate of 0.373-0.385 lb ai/A. The HAFT values were <0.070 ppm for nutmeat and 18.46 ppm for hay. The average combined residues were 0.06 ppm for nutmeat and 7.14 ppm for hay.

## E. REFERENCES

None

## F. DOCUMENT TRACKING

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